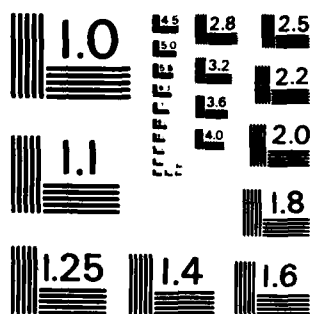


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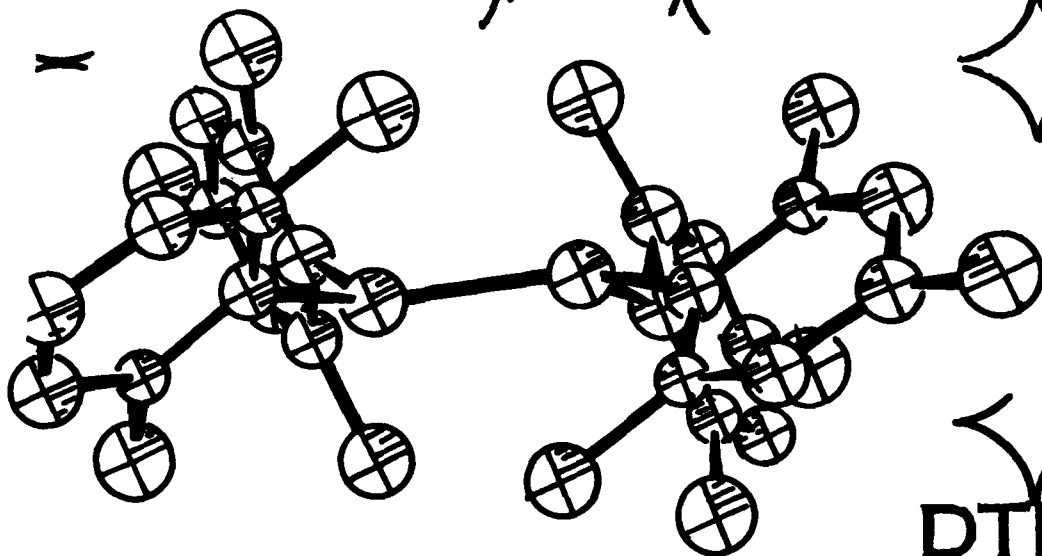
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# CHEMICAL & ATMOSPHERIC SCIENCES

AFOSR-TR- 83 - 0569

AFOSR FY-82

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## COVER

The picture in the middle depicts the spatial orientation from an X-ray crystallographic diagram of tetramesityldisilene molecule,  $(\text{Mes})_2\text{Si}=\text{Si}(\text{Mes})_2$ . This was the first organosilicon compound with a silicon to silicon double bond to be isolated and characterized. It was done by the research group of Professor Robert West of the University of Wisconsin working with Professor Joseph Michl of the University of Utah. This is just one of many important breakthroughs in organosilicon chemistry coming out of the AFOSR basic research program in chemical synthesis over the past twenty years. Due to the surge of interest in the past few years in organosilicon precursors to silicon carbide, silicon nitride, and other organometallic based ceramic materials, organosilicon research chemists have been interacting with ceramic materials research scientists and engineers in the AFOSR Chemistry Program. The uniform size of the circles in the background of the cover represents the ultimate in controlled powder geometry and chemistry, microstructure, and ultrastructure of the "best" performance ceramics. The articles in this book by Dr. Matuszko and Dr. Ulrich give further details of the organosilicon chemistry and ultrastructure ceramic processing interactions directed toward achieving new chemically derived materials. The cover art was designed by Capt Lee Myers.



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A review is presented of research efforts sponsored by the Directorate of Chemical and Atmospheric Sciences which have completed their period of support. Illustrated accounts resulting from the basic research programs in the Atmospheric and Chemical Sciences are highlighted. The Atmospheric Sciences is concerned with meteorology and upper atmospheric structure and dynamics. The meteorology focuses on mesoscale meteorology, cloud physics, and atmospheric dynamics. The Chemical Sciences deal with Chemical Techniques, Chemical Structures, Surface Chemistry, Chemical Dynamics, and Synthesis and Properties of Materials.		

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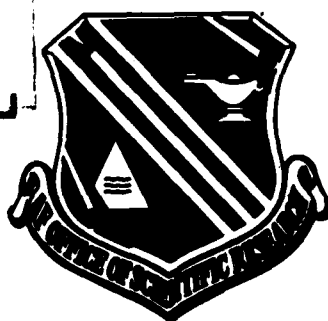
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27TH AFOSR  
 CHEMICAL & ATMOSPHERIC SCIENCES  
 PROGRAM REVIEW  
 FY82



WILLIAM G. THORPE & LEE E. MYERS, EDITORS  
 IRIS M. CROSS, MANAGING EDITOR

JUNE 1983

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR)  
 DIRECTORATE OF CHEMICAL AND ATMOSPHERIC SCIENCES  
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 WASHINGTON, D. C. 20332

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#### EDITORS' FOREWORD

A number of format changes have been made to the Chemical and Atmospheric Sciences Review over the last two years. Last year, we included for the first time short descriptions of the Air Force in-house laboratory programs in basic chemical and atmospheric sciences. We also introduced a constant dollar chart tracing Air Force support of basic chemical research over the last two decades. This year, we have organized the completed project summaries and active research programs by program manager. We feel this will help the users of the yearbook in locating the material most relevant to their interests. The program managers' articles are now intended to inform the reader about both our current program and our near-term plans. We hope these changes are useful and we invite your comments and suggestions on methods to further improve our Chemical and Atmospheric Sciences Review. A copy of AFSC Form 459 is included inside the front cover for this purpose.

The editors wish to thank all of the Directorate of Chemical and Atmospheric Sciences staff for their assistance and timely submission of material for this tome. Special thanks go to our secretarial staff for the long hours and dedication to completion of this year's review.

William G. Thorpe

Lee E. Myers

## MISSION

The Directorate of Chemical and Atmospheric Sciences of the Air Force Office of Scientific Research has the mission to encourage and support fundamental research designed to increase knowledge and understanding to stimulate the recognition of new concepts, and to provide for early exploitation of their military implications.

The Directorate obtains and maintains for the Air Force a diversified program of research at in-house laboratories as well as extramurally at university and industrial laboratories. The Directorate also functions as a dynamic interface between the Air Force and the scientific community, ensuring the free, full, and constant interchange of ideas from each to the other through publications, personal contacts, meeting attendance, and sponsored symposia. In these ways, the Directorate helps the Air Force maintain technological superiority.



DEPARTMENT OF THE AIR FORCE  
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)  
BOLLING AIR FORCE BASE, DC 20332

June 1983

TO: FRIENDS OF AFOSR

With the final stages of preparation of the 27th Chemistry Program Review, we continue a process that began in 1951. I cannot resist the temptation to reflect on that span of time and its impact on our organization. There have been major changes in leadership, administrative structure, scope of responsibility, and style of operation. However, we in the chemistry program are unique in AFOSR with our careful memory of the past. Our "style" has continuously evolved to meet changing circumstances with full knowledge of what has worked before. More importantly, examination of past experience reveals that our ultimate purpose has never changed at all. It remains the facilitation of research achievement of the highest possible quality and highest possible impact on future Air Force technology. The first Director of Chemical Sciences, Amos Horney, got that concept across to me in 1967 during my first week as a program manager.

Sincerely,

*Donald L. Ball*

DONALD L. BALL  
Director of Chemical and  
Atmospheric Sciences

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ATMOSPHERIC SCIENCES

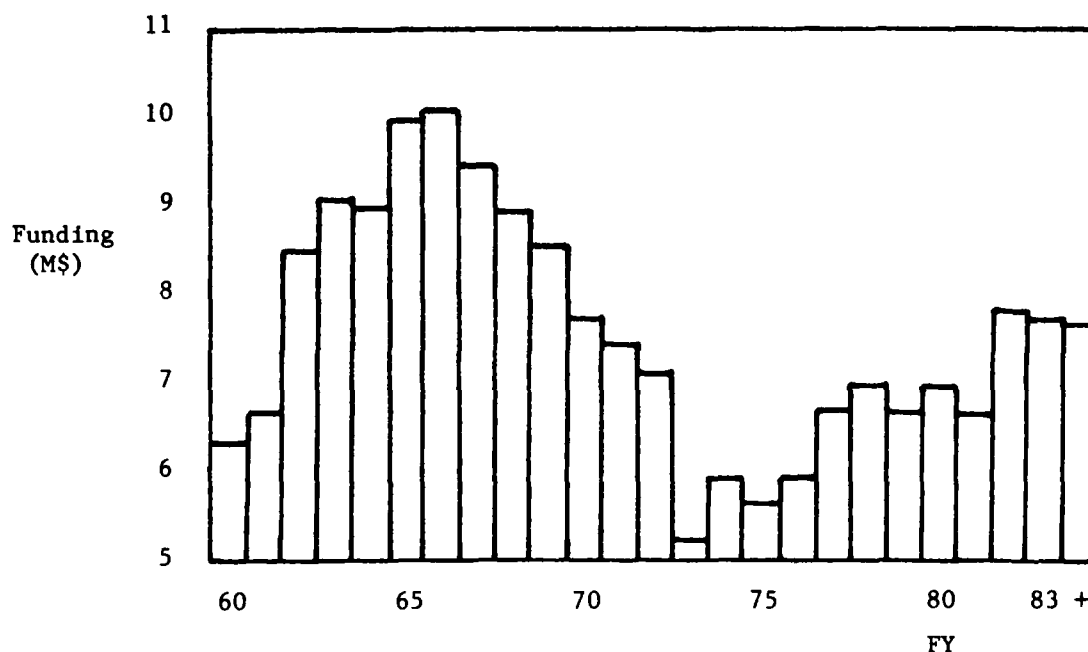
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Washington, D.C. 20057

Recent Chemistry Funding  
1983 Dollars\*



\* 1983 basis year

+ projected budget and inflation

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FY 82 CHEMISTRY PROGRAM STATISTICS

Total number of proposals received. . . . .	322
Total number of inquiries received. . . . .	267
New work efforts initiated. . . . .	74
Renewals. . . . .	60
Proposals declined. . . . .	148
Proposals withdrawn . . . . .	10
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## CONFERENCES AND SYMPOSIA

The following conferences and symposia were held during FY 82 with funds provided in part or wholly by the Directorate of Chemical and Atmospheric Sciences as a means of furthering areas of scientific research of particular interest to the Air Force.

### 1982 Gordon Research Conference on Polymers (West)

Drs. W. MacKnight and D. J. Meier  
Ventura, California  
11-15 January 1982

### 1982 Gordon Research Conference on Electrochemistry

Drs. Ted Kuwana and Halina Wroblowa  
Ventura, California  
17-22 January 1982

### Workshop on Hygroscopic Aerosols

Dr. L. H. Ruhnke  
Naval Research Laboratory  
Washington, DC 20375  
April 1982

### Symposium on Double Layer Phenomena - 161st Meeting of the Electrochemical Society

Dr. Douglas Henderson  
Montreal, Canada  
9-14 May 1982

### Fourth Symposium on Applied Surface Analysis

Dr. John T. Grant  
University of Dayton  
Dayton, Ohio  
2-4 June 1982

Eleventh International Laser Radar Conference

Dr. J. Weinman  
University of Wisconsin  
Madison, Wisconsin  
12-15 June 1982

1982 Gordon Research Conference on Molecular Electronic Spectroscopy

Dr. Robin M. Hochstrasser  
Brewster Academy  
Wolfeboro, New Hampshire  
9-13 August 1982

International Conference on Time-Resolved Vibrational Spectroscopy

Dr. George Atkinson  
Lake Placid, New York  
16-20 August 1982

1982 Gordon Research Conference on Organometallic Chemistry

Dr. I. Mador  
Proctor Academy  
Andover, New Hampshire  
16-20 August 1982

1982 Gordon Research Conference on Vibrational Spectroscopy

Dr. Richard P. Van Duyne  
Brewster Academy  
Wolfeboro, New Hampshire  
23-27 August 1982

Third International Conference on Vibrations at Surfaces

Drs. H. Morawitz and D. J. Auerbach  
Asilomar, California  
1-4 September 1982

ACTIVE RESEARCH EFFORTS

As of 1 Oct 1982

CHEMICAL TECHNIQUES - DENTON W. ELLIOTT

Surface Processes and Trace  
Analysis Using Solid Electrodes  
AFOSR-83-0004

Stanley Bruckenstein  
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Molten Salt Electrochemical  
System  
AFOSR-80-0173

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Electrosorption of Organic  
Molecules  
AFOSR-80-0262

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Evaluation of Chemical and Atmos-  
pheric Sciences Research Relevant  
to Current and Projected U.S. Air  
Force Interests  
F49620-81-C-0085

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High Energy Density Non-Aqueous  
Battery System  
AFOSR-82-0111

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Wilberforce, OH 45384

Synthesis Structure and  
Reactivity of Molecules Attached  
to Electrode Surfaces  
AFOSR-81-0149

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Santa Barbara, CA 93106

Electrocatalysis of Oxygen Using  
Water Soluble Metal Porphyrins  
and Chemically Modified Porphyrin  
Electrodes  
AFOSR-78-3672

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Electrochemistry and Electrochemical  
Methodology in Molten Salts  
AFOSR-81-0007

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Fast Protonic Conducting Solid  
Electrolytes  
AFOSR-82-0221

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Correlation of Electrode Kinetics  
with Surface Structure  
AFOSR-80-0271

Michael J. Weaver  
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Innovative Detection Separation  
and Sampling Techniques for Trace  
Analysis by Gas Chromatography  
AFOSR-80-0011

Robert E. Sievers  
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Atomic and Molecular Gas Phase  
Spectrometry  
F49620-80-C-0005

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Gainesville, Florida 32611

Secondary Ion Mass Spectrometry  
Studies of Solids and Surfaces  
AFOSR-82-0057

Nicholas Winograd  
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Pennsylvania State University  
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SURFACE CHEMISTRY - CAPTAIN LEE E. MYERS

A Mechanistic Study of Nitro-  
methane Decomposition on Ni  
Catalysts  
AFOSR-82-0099

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Reactions of Organic Molecules on  
Metal Surfaces  
AFOSR-82-0302

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Picosecond Laser Studies of  
Energy Transfer in Molecules  
on Surfaces  
AFOSR-ISSA-82-00050

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High Resolution Electron Energy  
Loss Studies of Chemisorbed  
Species on Aluminum and Titanium  
AFOSR-80-0154

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Theoretical Studies of Laser-Induced Molecular Rate Processes: Topics in Line Broadening and Spectroscopy  
AFOSR-82-0046

Molecular Order and Solidification Processes in Organic Liquids and Solutions  
AFOSR-80-0166

Time-Temperature Studies of High Temperature Deterioration Phenomena in Lubricant Systems: Synthetic Ester Lubricants  
F49620-80-C-0061

Structure of Solid Surfaces in Wear Situations  
AFOSR-81-0005

Theoretical Investigation of Homogeneous and Heterogeneous Reactions in the Chemical Vapor Deposition of Silicon from Silane  
AFOSR-82-0311

Surface Generation of Electronically Excited States of  $O_2$   
F49620-82-K-0025

The Role of Coupling Agents in Metal-Polymer Adhesion  
F49620-79-C-0085

Chemistry of Non-Equilibrium Film Deposition  
F49620-81-C-0074

Structure of Molecular Adsorbates on Surfaces  
AFOSR-82-0133

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CHEMICAL STRUCTURES - DR. DONALD R. ULRICH

Large Molecular Diffusion and  
Interfacial Effects in Oriented  
Polymers  
AFOSR-82-0290

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Light Scattering Studies of  
Molecular Dynamics in Molecular  
Crystals, Liquid Crystals, and  
Polymers for Applications in  
Chemical Defense  
AFOSR-82-0122

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Structural Electronic Relation-  
ships in Polymeric Solids  
AFOSR-80-0038

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Pulsed Microwave Characterization  
of Conducting Polymers  
AFOSR-82-0184

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Physical and Morphological  
Properties of Polymers  
AFOSR-82-0009

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TICA Study of High-Temperature  
Thermoplastics  
AFOSR-82-0301

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Ultrastructure Processing and  
Environmental Stability of  
Advanced Structural and Elec-  
tronic Materials  
F49620-80-C-0047

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International Conference on  
Ultrastructure Processing of  
Ceramics, Glasses, and Composites  
AFOSR-82-0293

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NMR Study of Disordered Materials  
under Extreme Conditions of Pres-  
sure and Temperature  
AFOSR-81-0010

Effect of Structure on Physical  
Properties of Polymers  
AFOSR-80-0101

An Approach to Molecular Composites  
AFOSR-79-0080

Preparation & Properties of  
Halide Glasses and Glass-Polymer  
Composites  
AFOSR-80-0059

High-Performance Polymeric Materials  
AFOSR-83-0027

Surface Chemistry and Structural  
Effects in the Stress Corrosion  
of Glass and Ceramic Materials  
AFOSR-82-0013

Molecular Mechanics of Polymeric  
Interactions in Relation to  
Chemical Defense  
AFOSR-82-0118

Microstructure of Amorphous and  
Semi-Crystalline Polymers  
AFOSR-81-0011

Polybenzothiazoles - Synthesis  
and Characterization  
F49620-81-K-0003

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MOLECULAR DYNAMICS - MAJOR WILLIAM G. THORPE

Rates of Intramolecular Con-  
versions Over Barriers  
AFOSR-80-0046

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Energy Disposal in Ion-Molecule  
Reactions  
AFOSR-82-0035

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Study in Molecular Lasers  
AFOSR-81-0028

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Ion Photofragment Spectroscopy:  
Structure and Dissociation of  
Molecular Ions  
F49620-81-K-0006

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Vibrational Relaxation Rates and  
Pathways in Highly Excited  
Molecules  
AFOSR-82-0244

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Chemiluminescence and Laser  
Induced Fluorescence of Boron  
Atom Reactions  
AFOSR-80-0061

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A Molecular Orbital Study of  
Atmospherically Important Cluster  
Ions  
AFOSR-82-0198

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Collisional Energy Exchange in  
Polyatomic Molecules  
F49620-80-C-0026

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Sequential Excitation Preparation of  
Molecular Energy Levels with  
Special Structural and Chemical  
Properties  
AFOSR-80-0254

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Massachusetts Institute of  
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Cambridge, MA 02139

Spectroscopic Studies of the  
Products of the Reactions of  
Noble-Gas Atoms  
AFOSR-79-0089

Theoretical Study of the Ener-  
getics and Dynamics of High  
Energy Inelastic Collision  
Processes  
F49620-80-C-0017

Energy Disposal in Electronically  
Excited Halogen Atoms and  
Molecular Oxygen  
AFOSR-78-3513

Measurement of Rate Constants of  
Elementary Gas Reactions of  
Importance to Upper Atmosphere  
and Combustion Systems  
AFOSR-80-0207

Computer Modeling of Pulsed  
Chemical Lasers  
AFOSR-80-0003

Spectroscopic Determination of  
Intermolecular Potentials of Gas  
Laser Components and of Major  
Atmospheric Constituents  
AFOSR-82-0036

Theoretical and Experimental  
Studies in Reactive Scattering  
AFOSR-82-0341

State-Resolved Dynamics of Ion-  
Molecule Reactions in a Flowing  
Afterglow  
F49620-83-C-0013

Analysis and Prediction of  
Experimental Results for  
Elementary Molecular Processes  
AFOSR-81-0030

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Study of Singlet Oxygen -  
Pentavalent Phosphorus Reactions  
F49620-82-C-0045

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Studies on Singlet Delta  
Oxygen  
AFOSR-82-0199

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Energetic and Collision Dynamics  
of Electronic Transition Laser  
Systems  
F49620-81-C-0097

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Electronically Excited Molecular  
Oxygen  
AFOSR-79-0088

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Nanosecond IR Spectroscopy  
and Vibrational Enhancement of  
Chemical Reactions  
AFOSR-82-0031

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The Molecular Dynamics of Reactions  
Forming Electronically Excited  
Products  
AFOSR-81-0027

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Chemical Kinetic Studies Involving  
NF and PF Radicals  
AFOSR-78-3507

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Computational Study of Nonadiabatic  
Effects in Atom-Molecule Reactive  
Scattering  
F49620-81-C-0046

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Experimental and Theoretical  
Studies of Molecular Dynamics  
AFOSR-81-0029

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Theory and Experiments on Chemical  
Dynamics and Instabilities  
AFOSR-81-0125

Nonlinear Interactions Between  
the Pumping Kinetics, Fluid  
Dynamics and Optical Resonator  
of CW Fluid Flow Lasers  
AFOSR-80-0133

Reactions of Laser-Generated  
Free Radicals at Semi-Conductor  
Surfaces  
AFOSR-83-0007

Studies of Energy Storage and  
Transfer  
AFOSR-82-0037

Laser Kinetic Spectroscopy of  
Unimolecular and Bimolecular  
Processes in the Gas Phase  
AFOSR-83-0022

A First Principles Approach to  
Electronic Energy Transfer Processes  
in Reactions of the Form  $Me + O-A =$   
 $MeO + A$   
AFOSR-79-0073

State Identification of Reaction  
Products  
AFOSR-81-0053

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CHEMICAL REACTIVITY AND SYNTHESIS - DR. ANTHONY J. MATUSZKO

Distibines, New One-Dimensional  
Materials  
AFOSR-81-0099

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New Approaches to the Synthesis  
of Novel Organosilanes  
AFOSR-80-0239

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New Approaches to Functionalized  
Fluorocarbons  
AFOSR-80-0259

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A New Approach to Highly  
Fluorinated Lubricants  
AFOSR-82-0084

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Development of Practical MO  
Techniques for Prediction of the  
Properties and Behavior of  
Materials  
AFOSR-79-0008

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Picosecond Laser Studies of Excited  
State Proton and Electron Transfer  
Phenomena  
AFOSR-81-0009

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Quantum-Theoretical Studies of  
Nerve Agents and Vesicant  
Compounds  
AFOSR-82-0100

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Ground and Excited State  
Reactions of Phosphonofluoridic  
Acids and Esters and Their  
Isomers  
AFOSR-82-0190

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Structural and Synthetic  
Organosilicon Chemistry  
AFOSR-81-0185

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Polyphosphorus Compounds Contain-  
ing Phosphorus-Nitrogen Bonds  
AFOSR-81-0051

An Approach to Molecular Composites  
AFOSR-79-0080

Studies of Polymer-Bound  
Macrocyclic Polytertiary  
Phosphines  
AFOSR-79-0090

Synthesis of Novel Fluorine  
Compounds - New Experimental  
Challenges in Elemental Fluorine  
Chemistry  
AFOSR-82-0197

Fabricable Polymers for Use Under  
Extreme Conditions  
AFOSR-82-0007

Mechanisms and Kinetics of  
Diphthalocyanine Electrode  
Processes  
F49620-80-C-0060

Synthesis of Novel Nitrogen and  
Phosphorus Heterocycles  
F49620-82-C-0021

Potential Energetic Materials  
Formed from Coupling of Sub-  
stituted Halo-S-Triazines  
AFOSR-82-0191

Basic Research in Novel Inorganic  
Reagents and Fluorocarbon  
Chemistry  
F49620-81-C-0020

Organosilicon Compounds:  
Monomers and Polymers  
AFOSR-83-0003

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Synthesis of Difluoraminoxy-,  
Difluoramino- or Fluorodiazonium-  
Containing Materials  
AFOSR-82-0247

Properties of Reactive Species  
Generated at High Temperatures  
and Their Low Temperature Reactions  
to Form Novel Substances  
AFOSR-82-0195

Compounds Containing Hetero-  
nuclear Metal-Metal Bonds  
AFOSR-82-0070

Theoretical Study of Penta-  
valent Phosphorus  
AFOSR-82-0114

Structural and Dynamic Studies  
of Materials Possessing High  
Energy Content  
AFOSR-81-0013

Chemistry of New Silicon Con-  
taining Polymers and Triply Bonded  
Silicon Intermediates  
AFOSR-82-0333

Chemical Reactions and Properties  
of Organosilicon Compounds  
Related to New Materials  
AFOSR-82-0067

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ATMOSPHERIC SCIENCES - LT COL TED S. CRESS

Behavior of the Atmosphere  
in the Desert Planetary Boundary  
Layer  
AFOSR-82-0285

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Fabry-Perot Determinations of  
Equatorial F-Region Neutral  
Winds and Temperatures  
AFOSR-82-0055

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MITHRAS Magnetosphere-  
Ionosphere-Thermosphere Radar  
Studies Using Three High-Latitude  
Incoherent-Scatter Stations  
F49620-81-C-0042

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Studies of the Auroral Zone  
Ionosphere Using the MITHRAS  
Data Base  
AFOSR-83-0002

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Dynamic-Chemical Coupling in the  
Mesosphere and Lower Thermosphere  
AFOSR-81-0090

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High Time Resolution Studies  
of the Auroral Ionosphere  
AFOSR-82-0093

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A Numerical and Observational  
Investigation of Gravity-Wave/  
Mean Flow Interactions in the  
Atmosphere  
AFOSR-82-0125

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Global Atmospheric Waves  
AFOSR-82-0052

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Studies of Extratropical Cyclonic  
Storms; The CYCLES Project  
AFOSR-ISSA-83-00018

A Laboratory Study of Aircraft  
Precipitation Static Charging  
AFOSR-81-0189

A Theoretical Framework for  
Examining Geographical Variability  
in the Microphysical Mechanisms of  
Precipitation Development  
AFOSR-82-0179

Construction of University of  
Missouri-Rolla's Full Scale Cloud  
Simulation Chamber  
F49620-80-C-0090

Analysis of the NOAA Alaskan MST  
Radar System Data  
AFOSR-80-0020

Light Scattering and Absorption  
Properties of Ice Clouds for Visible  
and Infrared Laser Wavelengths  
F49620-79-C-0198

A Study of the Effects of  
Triggered Lightning  
AFOSR-82-0206

Vertical Wind Speeds Observed by  
the Poker Flat, Alaska, MST  
F49620-82-C-0029

Investigation into the Nature of  
Snowflake Aggregation in the  
Vicinity of the Melting Layer  
in Stratiform Clouds  
AFOSR-82-0173

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Effects of Mountain Ranges on  
Mesoscale Systems Development  
AFOSR-82-0162

High Time Resolution Thermospheric  
Temperature and Wind Studies in the  
Arctic  
AFOSR-80-0240

A Systematic Study of Light  
Scattering by Irregularly Shaped  
Particles  
AFOSR-MIPR-82-00052

Rainfall Studies Using the  
Differential Reflectivity Radar  
Techniques  
AFOSR-ISSA-82-00043

Upper Atmospheric Structure  
and Dynamics  
AFOSR-ISSA-82-0042

Latitudinal Variations of Auroral  
Zone Ionization Distributions  
F49620-80-C-0014

Phase Fluctuations of Trans-  
ionospheric Signals under  
Multiple Scattering Conditions  
F49620-82-C-0058

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Air Force Laboratory Chemical Sciences

Research Projects

1. TITLE: Physical Chemistry and Electrochemistry

2. PRINCIPAL INVESTIGATOR: Capt John L. Williams  
Frank J. Seiler Research Laboratory  
Air Force Academy, CO 80840

3. ABSTRACT OF OBJECTIVES:

Provide scientific basis for the development of high current density and high energy density electrochemical power supplies.

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1. TITLE: Energetic Materials Chemistry Research

2. PRINCIPAL INVESTIGATOR: Dr. John S. Wilkes  
Frank J. Seiler Research Laboratory  
Air Force Academy, CO 80840

3. ABSTRACT OF OBJECTIVES:

Synthesis of new oxidizers based on tetrazines is being accomplished utilizing novel synthetic chemistry. Xenon difluoride is being investigated as a reagent for preparation of such compounds. Understand the thermochemical and photochemical decomposition mechanisms of explosives. Discover new low-hydrogen content explosives.

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1. TITLE: Upper Atmosphere Chemistry

2. PRINCIPAL INVESTIGATOR: Dr. John F. Paulson  
Air Force Geophysics Laboratory  
Hanscom AFB, MA 01731

3. ABSTRACT OF OBJECTIVES:

Measure rate coefficients for reactions between atmospheric ion species and neutral molecules as a function of temperature. Measure the optical emission produced in such reactions. Study photoabsorption processes in atmospheric neutrals and ions. Study the collisional and radiative quenching reactions for photoexcited species. Measure rate coefficients for electron attachment, ion-electron recombination, and positive ion-negative ion mutual neutralization. Calculate the product energy levels and reaction hypersurfaces for ion-electron and ion-neutral reactions important as sources of IR/optical emission.

1. TITLE: Plume Atmosphere Interactions

2. PRINCIPAL INVESTIGATOR: Mr. Alfred Rahbee  
Air Force Geophysics Laboratory  
Hanscom AFB, MA 01731

3. ABSTRACT OF OBJECTIVES:

Investigate and measure vibrational excitation cross sections for high-velocity collisions of major rocket plume species with atmospheric species. The results are ultimately used in plume analysis and prediction.

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1. TITLE: Synthesis and Mechanism of Propellant Ingredients

2. PRINCIPAL INVESTIGATOR: Major Scott Shackelford  
Air Force Rocket Propulsion Laboratory  
Edwards AFB, CA 93523

3. ABSTRACT OF OBJECTIVES:

Investigate chemical syntheses designed to define specific new chemical synthetic transformations, to achieve novel chemical structures, to improve overall synthetic routes to known candidate propellant ingredients, to produce new target compounds, and to provide on-going syntheses of novel model compounds required for investigations in complementary in-house chemical research programs. Synthesize modified or new tough, cureable, high energy polymer binder candidates for smokeless propellants, high solid loaded formulations and/or high performance hybrid fuels with vastly improved mechanical, physical, and chemical compatibility characteristics including a thermochemical stability 200°C and a glass transition temperature as low as -55°C. Synthesize nonenergetic and energetic copolymers of different molecular weight distribution ranges for subsequent curing into monomodal, bimodal, and polymodal, binder networks. Investigation of Mark's generalized new multimodal concept for improved stress/strain properties as applicable for propellant binder systems. Determine the detailed initial and rate-controlling thermochemical mechanisms of propellant ingredient decomposition reactions as applicable to precombustion conditions and to establish systematic relationships between key initially controlling steady-state decomposition mechanisms and molecular structure as applied to chemical stability, compatibility, and decomposition rate modification. In-situ elucidation of the ingredient rate-determining bond rupture and mechanism responsible for controlling the global propellant burn rate process. Determine the degree of kinetic versus thermodynamic control in propellant ingredient burning processes and in selected propellant formulations. Elucidate important chemical interactions between specific formulated propellant ingredients.

1. TITLE: Surface Phenomena

2. PRINCIPAL INVESTIGATOR: Dr. Trice W. Haas  
Air Force Wright Aeronautical Laboratories  
Materials Laboratory  
Wright-Patterson AFB, OH 45433

3. ABSTRACT OF OBJECTIVES:

Elucidate the basic chemical and physical factors affecting the control, activation, lifetime, and poisoning of various types of low work function cathodes (oxide, dispenser, matrix) for use in travelling wave tubes. Determine the surface chemical factors which control the growth, perfection, and electrical characteristics of thin film silicon grown epitaxially on sapphire substrates. Determine epitaxial relationships of silicon films on cubic stabilized zirconia substrates, investigate interface chemistry resulting from the epitaxy process and measure silicon film electrical properties.

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1. TITLE: Fluids and Lubricants Synthesis

2. PRINCIPAL INVESTIGATOR: Dr. Christ Tamborski  
Air Force Wright Aeronautical Laboratories  
Materials Laboratory  
Wright-Patterson AFB, OH 45433

3. ABSTRACT OF OBJECTIVES:

Perform thermal degradation studies on polyalkylbenzene compounds under a) non-oxidative and b) oxidative conditions. Perform molecular structure versus physical and chemical properties studies in order to optimize desirable chemical structures possessing optimum properties. Initiate a program on the synthesis of silahydrocarbon compounds via non-organometallic (organolithium and Grignard reagents) methods.

1. TITLE: Basic Factors in the Synthesis of Macromolecular Materials

2. PRINCIPAL INVESTIGATOR: Dr. Richard L. Van Deusen  
Air Force Wright Aeronautical Laboratories  
Materials Laboratory  
Wright-Patterson AFB, OH 45433

3. ABSTRACT OF OBJECTIVES:

Provide the basic scientific knowledge about the synthesis and behavior of polymeric materials that will provide new base materials and knowledge of their physical and chemical properties, mechanical behavior, and composition and morphology for future development of new improved nonmetallic structural materials for advanced aircraft systems.

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1. TITLE: Electrochemistry

2. PRINCIPAL INVESTIGATOR: Dr. D. Fritts  
Air Force Wright Aeronautical Laboratories  
Aero-Propulsion Laboratory  
Wright-Patterson AFB, OH 45433

3. ABSTRACT OF OBJECTIVES:

Elucidate the life limiting mechanisms at nickel electrodes associated with mechanical alteration, corrosion of plaque material, and cell thermal phenomena. Investigate self-discharge mechanisms, discharge rate capability, and passivation while enhancing the safety of primary high energy density batteries. Evaluate low temperature molten salt electrolytes and ambient temperature non-aqueous electrolytes for potential application in high energy density rechargeable batteries. Study the electrochemistry associated with very high current discharge (for short time periods) delivered by either primary or rechargeable batteries. In the case of secondary cells, discharge currents would be greater than fifty times the normal rated load so that thermal control will also be investigated. Explore the electrochemical aspects of lithium rechargeability in combination with various potential cathodes.

1. TITLE: Laser Kinetics

2. PRINCIPAL INVESTIGATOR: Dr. Leroy E. Wilson  
Air Force Weapons Laboratory  
Kirtland AFB, NM 87117

3. ABSTRACT OF OBJECTIVES:

Theoretically and experimentally determine the physical chemistry parameters of rotational energy transfer rate, quenching rate, V-V exchange, and line broadening parameters of an optically pumped transfer cell. Experimentally determine the HF/DF high vibration state relaxation rate constants using double resonant techniques and develop new experimental and theoretical techniques for determining state to state reaction rates. Model energy transfer kinetics, including rotational non-equilibrium effects. Experimentally and analytically determine limiting processes when radiative times become comparable to kinetic times. Experimentally determine limiting processes in high gain lasers, such as superfluorescence, supersaturation, and parasitic oscillations. Measure the effect of anomalous dispersion on the output beam quality of a high energy chemical laser during power broadening.

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1. TITLE: Electronic Transition Chemical Laser Concepts

2. PRINCIPAL INVESTIGATOR: Dr. Steve Davis  
Air Force Weapons Laboratory  
Kirtland AFB, NM 87117

3. ABSTRACT OF OBJECTIVES:

Identify and explore new candidates for development of efficient, high-energy, electronic transition, gas phase chemical lasers.



Air Force Geophysics Laboratory  
Hanscom AFB, MA 01731

Atmospheric Sciences

Research Projects

1. TITLE: Molecular and Aerosol Properties of the Atmosphere
2. PRINCIPAL INVESTIGATOR: Dr. George A. Vanasse
3. ABSTRACT OF OBJECTIVES:

Obtain laboratory high-resolution, ambient and high-temperature data of atmospheric constituents, and perform balloon-borne measurements of stratospheric emission using a high resolution cryogenic interferometer. Conduct research leading to the development of more sensitive techniques for improving the accuracy of spectral and remote sensing measurements. The high-resolution data will be used to obtain improved molecular parameters for use in the theoretical spectroscopy effort of the task, and also for updating the transmission/emission codes. Develop techniques to compute molecular absorption/emission line widths and shapes, and compare results with laboratory and field measurements. Develop an understanding of the intermolecular forces and statistics of molecular collision processes; and also new methods for calculating atmospheric spectra from a set of known absorption line parameters and line shapes. Develop models of the optical properties of aerosols in order to calculate such parameters as beam attenuation, angular scattering intensities, polarization, path radiance and contrast transmission. Also perform experimental and theoretical studies in order to correlate aerosol particle refractive index, size distribution, and concentration with meteorological and environmental conditions.

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1. TITLE: Upper Atmosphere Composition
2. PRINCIPAL INVESTIGATOR: Dr. Rocco S. Narcisi
3. ABSTRACT OF OBJECTIVES:

Measure the ionospheric species present in the upper atmospheric D- and E-regions during solar-disturbed periods to determine upper atmospheric physical-chemical processes important to LF/VLF/HF communications. Develop models of ion/electron structure, physical-chemical processes and transport mechanisms in order to describe the twilight and daytime disturbed high-latitude ionosphere. Measure composition with high spatial resolution to provide understanding of the physical-chemistry and transport processes in the creation of ionospheric irregularities/scintillations in the equatorial, midlatitude and polar regions.

1. TITLE: Infrared Atmospheric Processes
2. PRINCIPAL INVESTIGATOR: Dr. R. A. Armstrong
3. ABSTRACT OF OBJECTIVES:

Study and define the processes that control infrared emissions in auroral and nuclear-disturbed atmospheres. Determine the spectral, spatial and temporal character of airglow infrared emissions with and without solar illumination.

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1. TITLE: Remote Ionospheric Mapping
2. PRINCIPAL INVESTIGATOR: Dr. J. R. Jasperse
3. ABSTRACT OF OBJECTIVES:

Develop quantitative methods for specifying the electron density profile from the analysis of particle, optical and electromagnetic wave data. Develop an understanding of the onset of plasma turbulence in the ionosphere and how the properties of the turbulent regions can be specified by remote measurements. Develop an understanding of how changes in the magnetosphere affect the state of the high-latitude ionosphere.

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1. TITLE: Atmospheric Dynamic Models
2. PRINCIPAL INVESTIGATOR: Dr. Chien-hsiung Yang
3. ABSTRACT OF OBJECTIVES:

Formulate a dynamic-numerical model of the moist atmosphere on a global scale to serve as a research vehicle to understand the dynamics and physics of the atmosphere. Understand and model medium (meso) scale dynamics and the interactions between this scale and both the larger and the smaller scale processes.

1. TITLE: Advanced Weather Satellite Techniques

2. PRINCIPAL INVESTIGATOR: Dr. K. R. Hardy

3. ABSTRACT OF OBJECTIVES:

Develop and test theories for the retrieval of meteorological information from satellite observations and to devise techniques for the incorporation of satellite data into numerical weather prediction models.

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1. TITLE: Global Ionospheric Dynamics

2. PRINCIPAL INVESTIGATOR: Dr. H. Carlson

3. ABSTRACT OF OBJECTIVES:

Determine the dominant physical processes driving temporal and spacial ionospheric variability over scales of concern to Air Force systems.

## CHEMICAL TECHNIQUES

Denton W. Elliott

Technical emphasis in this program is divided between detection and electrochemistry areas of research. In the first area, atomic and molecular spectrometric instrumentation are being developed along with methodologies to enable detection of ultra-trace and below concentrations. Local combustion diagnostics are being exploited to permit detection of gas species and flame temperatures. Selective and sensitive gas chromatographic techniques and ancillary methods are under observation for the improvement of sample collection procedures, new chromatographic media, and novel separation schemes.

In the electrochemical area, investigations of new electrode/electrolyte systems for high energy density and long storage life are being undertaken. The chemical and physical characterization of new materials for battery components is being exploited. It is the new materials area that special attention is being given.

At Oxford University, Professor J. B. Goodenough and Dr. P. G. Dickens have been involved in the design, preparation, and characterization of new materials for electrochemical cells. Special emphasis was placed on solid-solution cathodes for secondary batteries of high specific energy and power.

Secondary batteries rely on reversible chemical reactions at the electrodes. In conventional systems, cations are transported from the anode to the cathode during discharge, and chemical reaction at the cathode introduces a second crystallographic phase. The kinetics associated with propagation of the phase boundary limits the power output of the cell; materials mismatch across the phase boundary causes deterioration of the cathode on repeated discharge/charge cycles, particularly for deep cycles. In order to circumvent these two problems, two new approaches to cell design are under active development: (1) use of liquid electrodes and a solid electrolyte, typified by the high-temperature Na/S cell first proposed at the Ford Research Laboratories, and (2) use of a solid solution cathode - first investigated for electrochromic devices - typified by the Li/TiS<sub>2</sub> cell developed at Exxon Research Laboratories. A third alternative is to develop an all-solid-state battery utilizing a solid electrolyte and a solid-solution electrode. Electrolysis/fuel cells are similar to secondary batteries except that the fuel generated in the electrolysis (charging) mode may be shipped to a distant place to be consumed in the fuel-cell (discharge) mode, and half-cycles are useful in their own right. Solid electrolytes are well adapted to liquid and gas phases; conventional cells are plagued by corrosion problems at the high temperatures and pressures desired for low overvoltages. Fast O<sup>2-</sup>-ion conductors are sought for high-temperature electrolysis; fast H<sup>+</sup>-ion conductors for lower-temperature fuel cells.

Professor Goodenough and his group have come up with an invention that relates to an electrical device which includes a conductor of hydrogen cations ( $H^+$ -ion). The conductor is a pressed body of a metal oxide and water. The water content of the body being more than one-quarter in excess of that necessary to form the most hydrated hydrous oxide of the metal. The metal oxide is in the form of particles having an average size of under 500Å. The need for any excess of water arises from the fact that only the excess water forms surface groups on the particles, and a specified amount of excess is needed to ensure minimum continuous aqueous conducting pathways enveloping the particles; any lesser nominal excess tends to be all used up in stabilizing the particle surfaces. This invention is covered under U.S. Patent Application 12058.

Another invention which originated from the Oxford group's research is concerned with a method of preparing a high surface area form of  $LiCoO_2$ . This is covered under U.S. Patent Application 135222. It relates to ion conductors having the formula  $A_xM_yO_2$  and having the layers of the  $\alpha$ - $NaCrO_2$  structure, in which A is Li, Na, or K; M is a transition metal; X is less than 1 and Y is approximately equal to 1. The  $A^+$  cation vacancies in the ion conductor having been created by  $A^+$  cation extraction. Such ion conductors have potential application as solid-solution in electrochemical cells.

Conventional batteries rely on mass transport from one solid electrode to another through a liquid electrolyte. Chemical reaction at the cathode results in the formation of a new solid compound, and power densities are limited by the low mobilities of the interphase boundaries. Moreover, volume changes associated with the formation of a new phase cause degradation of the electrode. Two ways of meeting these problems have hitherto been proposed, namely use of the liquid electrodes separated by a solid electrolyte and use of a solid-solution cathode that is a mixed ionic/electronic conductor. The former requires operation at temperatures high enough to keep the electrodes molten; the latter permits low-temperature operation. The literature discloses compounds of such suitability for use in the latter, e.g. the layer compounds  $Li_xTiS_2$ .

The question arises as to what direction should be taken in the new electrochemical materials research program.

The potential technological significance of solid materials exhibiting fast ionic conduction is now well recognized; the new journal titled Solid State Ionics testifies to a growing activity in the field. Of particular interest are solid electrolytes and solid-solution electrodes.

Solid electrolytes act as separators and permit the use of either liquid or gaseous reactants to (or products from) an electrochemical cell. They also permit wider temperature and pressure variations than do liquid electrolytes. They are therefore of immediate interest for electrolysis/fuel cells, oxygen sensors, high-temperature secondary batteries and thermoelectric-power devices. Four specifications are essential for a technologically viable electrolyte:

- (1) Low-cost fabrication into dense "membranes"
- (2) Chemical stability in working environment
- (3) Ionic conductivity high enough for tolerable  $I^2R$  losses
- (4) An ionic transport number  $t_i = \sigma_i/\sigma$  approaching unity.

Difficulties in meeting the first of these specifications has prevented realization of a marketable Na-S battery based on Na -alumina despite intensive development programs. Lack of an adequate or appropriately located electrochemical "window" limits the choice of reactants/products that might be used with  $\text{Li}^+$ -ion conductor  $\text{Li}_3\text{N}$ . Unless extremely thin membranes can be used, the ionic conductivity at the operating temperature must approach that of a good liquid electrolyte at room temperature, which restricts ceramic materials to the "superionic" class. Finally, in order to keep the electronic conductivity much lower than the ionic conductivity, it is necessary to have not only a large electronic bandgap - compatible with an adequate electrochemical window, but also no oxidation or reduction of the solid under operating conditions. This constraint has been most difficult to fulfill in the case of  $\text{O}^{2-}$ -ion electrolytes.

Solid-solution (or insertion) electrodes are mixed ionic/electronic conductors suitable for reversible electrodes; mobile ions may be inserted or extracted electrochemically without changing the basic structure of the host matrix. This requirement is essential for high power and long cycle life.  $\text{PbO}_2$ , the cathode of a lead-acid battery, accepts protons reversibly, for example, but it suffers from a slow disproportionation reaction into  $\text{Pb}^{2+}$  and  $\text{Pb}^{4+}$  ions once the hydrogen concentration goes beyond a critical limit; it is this disproportionation reaction that cause the cathode to deteriorate if the battery stays for any time in deep discharge. Metallic transition-metal oxides or sulfides are known that avoid this problem. However, it is important to find transition-metal oxides (or sulfides) with not only suitable structures for the reversible insertion of a desired mobile cation, but also a redox couple that is tailored to fit the electrochemical window of the electrolyte to be used.

In order to obtain maximum utilization of a cathode, especially under high-power conditions, it is necessary to fabricate the electrode as an electrolyte-electrode composite in which the electrode materials consists of colloidal-size particles pressed into electrical contact with one another. In such a composite, the ionic conductivity of the electrolyte must generally be better than  $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$  at operating temperature, a requirement difficult to satisfy at room temperature in solid electrolytes. Moreover, all solid-solution electrodes tend to have some volume change on mobile-ion insertion, so all-solid composites may not sustain good ionic conductivity across the electrode/electrolyte interfaces on deep discharge/charge cycling. These considerations suggest the use of a liquid or polymeric electrolyte in the composite electrode, but perhaps in conjunction with a thin solid-electrolyte separator.

Although solid-solution electrodes have been developed for cathodes, they have not been used as anodes. This area needs wider exploration.

The technologies promised by fast ionic conductors have been disappointingly slow in maturing because an adequate range of materials has not been developed for suitable matching. There is a clear need to discover new ionic conductors, to obtain quantitative thermodynamic, structural and kinetic data on known ionic conductors, and to develop an adequate theoretical understanding of ionic-transport processes in fast ionic conductors.

## SURFACE CHEMICAL RESEARCH AT AFOSR

Captain Lee E. Myers

This past year has been one of change, with many new names appearing in the AFOSR Surface Chemistry program. Our move out of the fields of adhesion and lubrication is proceeding and will be concluded during FY 83. The development of a replacement program in thin films continues and appears to be nicely complementary to our older program in surface reactions. During the past year, the program in electromagnetic materials, which was to be initiated during FY 82, was dropped from consideration for funding within the chemistry directorate. Overall, our emphasis upon research which furthers the molecular understanding of structures of and processes occurring on solid surfaces has been given a solid basis with these program changes. This emphasis upon microscopic phenomena will continue over the coming years.

The surface reactions/reactivity research area has been sizeably expanded since last year's yearbook article was written. Five new programs were added to this research area during FY 82. This program remains the largest in AFOSR's surface chemistry task and is anticipated to experience further growth during FY 83. Its research topics include both static and dynamic aspects of surface reactions and include a wide variety of surface phenomena and materials. Emphasis has remained upon gas/surface dynamics, surface characterization, and surface reaction kinetics and mechanisms. The only programmed restriction applied to this research area is the omission of solar and petroleum related surface catalytic chemistry. Scientific quality and uniqueness will remain as essential factors for evaluation of proposals.

The research task on thin films was new with FY 82. A significant number of new research programs were initiated and some limited expansion is expected during FY 83. Problems involving thin films are found in many high technology fields such as electronic device development. One significant Air Force application of this technology is in high energy laser optical coatings. Emphasis in our program has been upon the fundamental understanding of various aspects of thin film science including film characterization, gas/thin film interaction and reactivity, substrate/thin film stability, film nucleation and growth, and intense light/thin film interactions.

The "initiative" programs at AFOSR have developed into our largest source of unencumbered research funds. Over the past two years, surface chemistry has benefited by involvement in two initiatives, chemical defense and space power and propulsion. It is hoped that our involvement with these programs will continue and expand to further strengthen the Air Force commitment to fundamental surface science research.

FY 82 saw two surface science meetings partially supported by our office, the 4th Symposium on Applied Surface Analysis held at the University of Dayton, Dayton, Ohio, and the Third International Conference on Vibrations



at Surfaces held at Asilomar, California. During FY 83, once again two surface science conferences will be partially supported, the 1983 Gordon Conference on the Dynamics of Gas-Surface Interactions to be held at Plymouth, New Hampshire and the Sixth International Summer Institute in Surface Science held at the University of Wisconsin, Milwaukee, Wisconsin.

1-3 December 1982 were the dates for the first combined Molecular Dynamics and Surface Chemistry Contractors' Meeting, held at the USAF Academy, Colorado. Although the number of surface science talks was small this year, initial reviews of the meeting are favorable and supportive of the joint meeting concept. Both Maj Thorpe and I look forward to continuing this association at next year's meeting to be held at the AF Geophysics Laboratory, Hanscom AFB, Massachusetts.

In conclusion, I would like to reiterate that this past fiscal year was one of considerable change in the AFOSR Surface Chemistry program. A total of nine new programs were brought into the Surface Chemistry task since the last yearbook was published. Although we look forward to a continuation of this trend, it is clear that further expansion will proceed at a considerably slower pace. Overall, the past year has been outstanding and the coming year appears to hold considerable promise for the Surface Chemistry task.

POTENTIAL IMPACT OF ULTRASTRUCTURE  
PROCESSING ON GOVERNMENT AND INDUSTRY

Dr. Donald R. Ulrich

The major problem that has led to the stagnation of ceramics in the United States has been the neglect of the role of chemistry. The focus of ceramics research has been on property control, structural development at the microstructural level, and densification through emphasis of fabrication methods and high temperature. The basis for these approaches has been derived from physics. For example, the various proposed theories for sintering have had their foundations in physics, chemical consideration not being taken into account. The result has been models that will predict the rate of sintering or the density for a specific material processed at a specific temperature and perhaps pressure, but not a model which has broad-based application. The result in the view of the observer is that ceramic science has travelled the complete circle back to our starting point of twenty years ago.

This has implications for the U.S. which strikes at the heart of both our economic and national security. There is no need to stress as a problem the interest and growing competition in ceramics from Japan, as well as our other Allies, who classify ceramics as a chemically derived material.

Ultrastructure processing refers to the manipulation and control of surfaces and interfaces during the earliest stages of formation at scales of 50-1000 Angstroms. Through chemical processes, the consequence will be a new generation of high performance structural and electromagnetic ceramic materials with predictable properties, lifetime reliability and environmental insensitivity. In applications where high performance is required, high temperatures and sophisticated fabrication processes alone are not sufficient to produce properties approaching theoretical values in structural ceramics. Achieving this goal will require the raw material control - controlled powder geometry and chemistry - which will result in controlled microstructure, and most importantly, controlled ultrastructure - homogeneous structures, extremely fine scale (100 Angstroms) second phases, and controlled surface compositional gradients (Figure 1).

The integrated approach using several fields of chemistry, such as organic or organometallic, surface, structural, physical and polymer, with ceramics is the key to success here. For example, the synthesis of controlled raw materials should start with the design of new molecules by the organic or organosilicon chemist, who interacts with the polymer chemist and ceramist for the conversion of the organic to a ceramic powder of controlled geometry, size and size distribution, and controlled surface and bulk chemistry.

Figures 2 and 3 show the approach that the Air Force Office of Scientific Research funded multi-investigator research program at the University of Florida has taken.

# ULTRASTRUCTURE PROCESSING

Figure 1.

## • SURFACE CHEMISTRY APPROACH TO HIGH PERFORMANCE CERAMICS

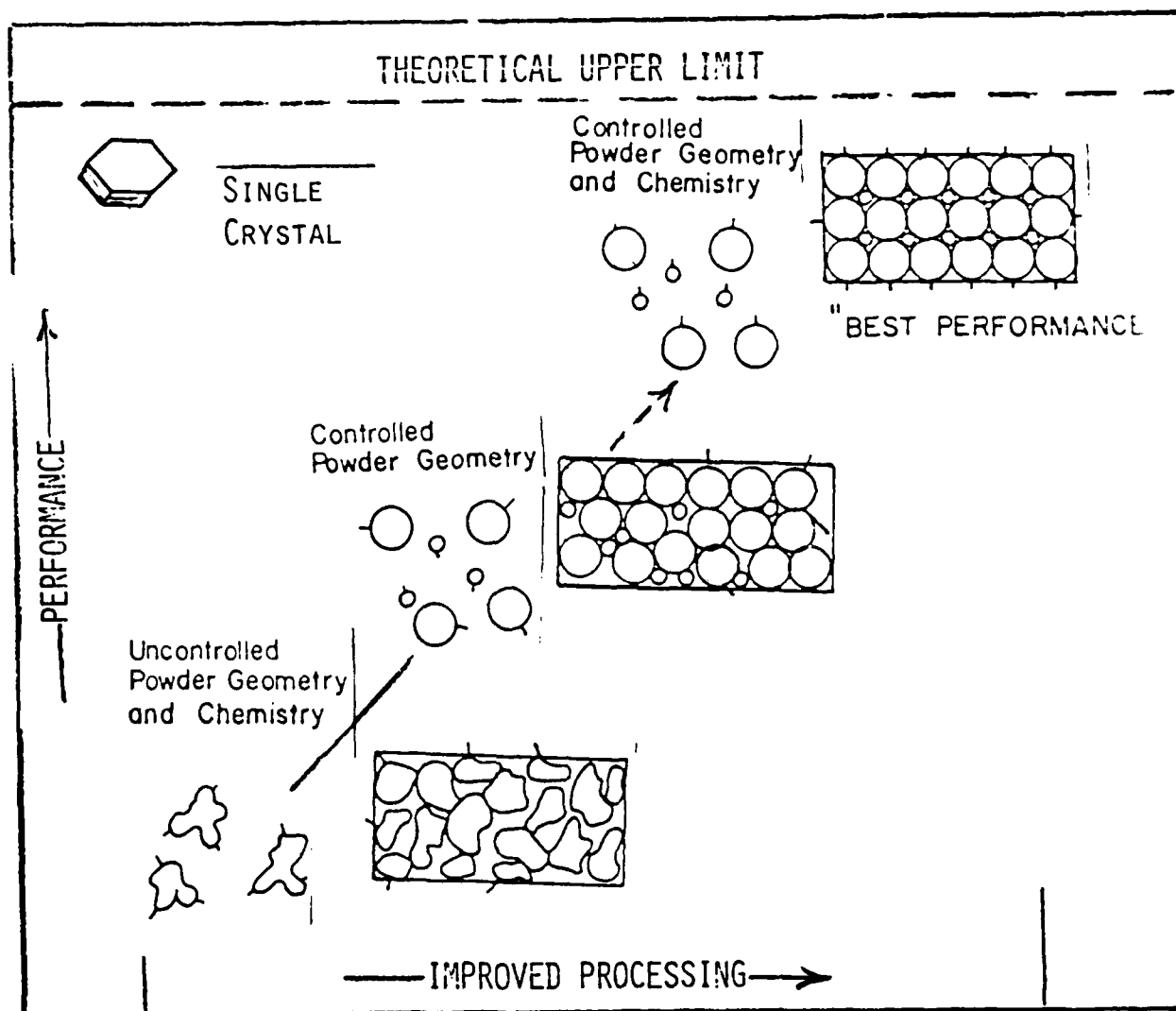


Figure 2 represents the approach that the program took in its early stages. Drs. Hench and Clark used glass and glass-ceramics as a model system for understanding more practical high performance materials. The microstructure and ultrastructure can be controlled by the proper temperature/time schedule with this particular model system. The glass itself is two component and its surface chemistry has been well

# ULTRASTRUCTURE PROCESSING OF HIGH PERFORMANCE CERAMICS

## GLASS/GLASS-CERAMICS—A Model System for Developing High Performance Ceramics

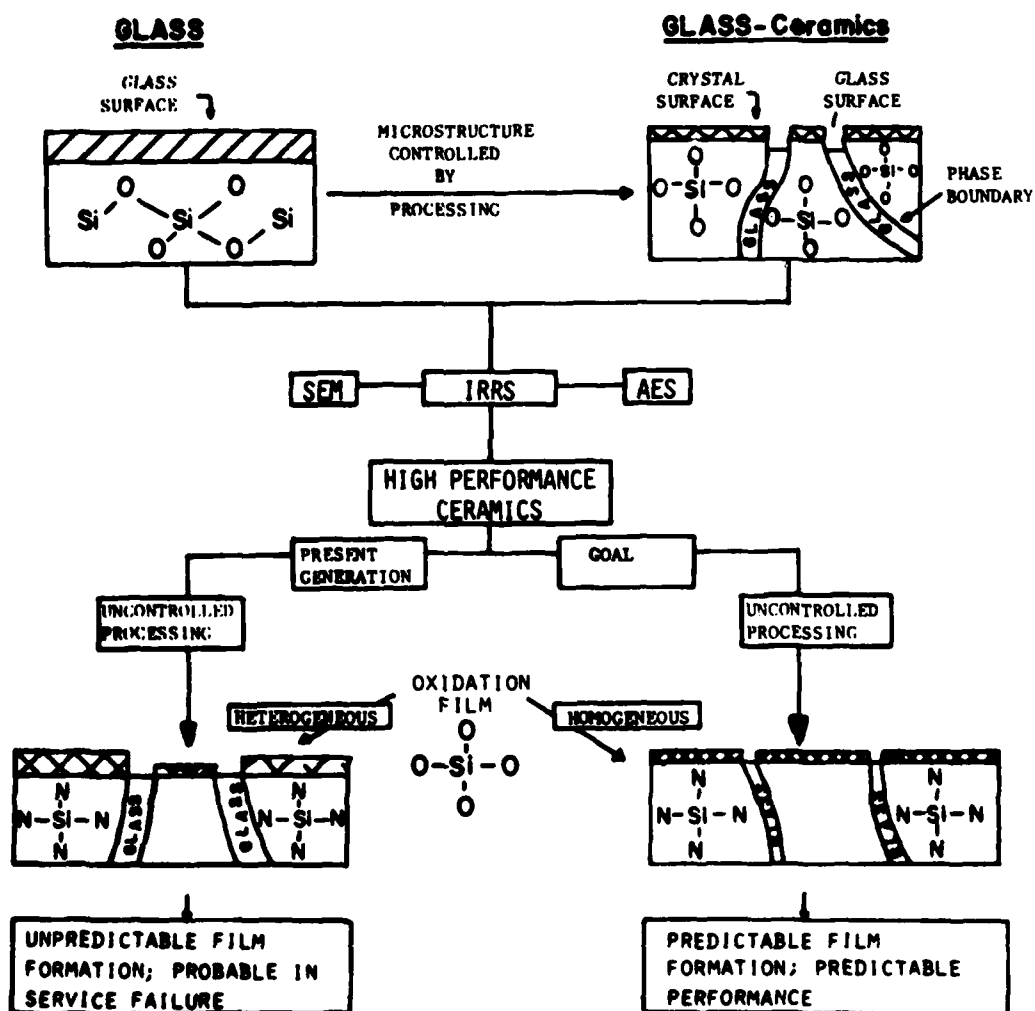
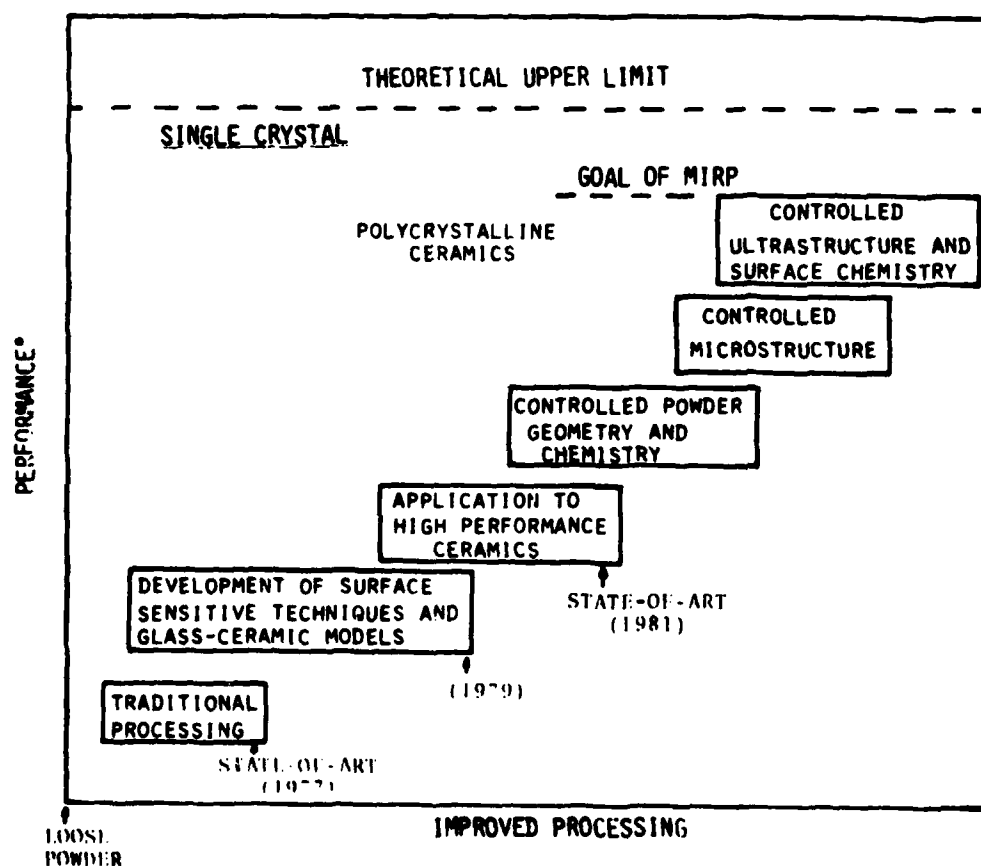


Figure 2.

# ULTRASTRUCTURAL PROCESSING OF HIGH PERFORMANCE CERAMICS

## APPROACH

### IMPROVED PERFORMANCE THROUGH CONTROLLED PROCESSING



\*MECHANICAL STRENGTH, CHEMICAL RESISTANCE, ENVIRONMENTAL STABILITY

Figure 3.

characterized with scanning electron microscopy, infrared reflection spectroscopy and auger electron spectroscopy. These techniques were specially developed for implementation of the surface chemistry approach to ultrastructure processing.

When the glass is crystallized, the crystals that form have the same composition as the glass, thus producing a fairly homogeneous ultrastructure (i.e., phase boundaries of compositions the same as the glass and crystals). The oxidation films and phase boundary that occur on high performance materials such as silicon nitride,  $\text{Si}_3\text{N}_4$ , have many similarities to the glass-ceramics. For this reason, Hench and his associates have been successful in applying the same approach that was used for glass-ceramics to the high performance ceramics. One other feature that this figure illustrates is homogeneous versus heterogeneous oxidation of the  $\text{Si}_3\text{N}_4$  surface. Controlled ultrastructure during processing will produce in-service uniform, thickness-limited surface oxidation films and phase boundaries with predictable and high performance, while uncontrolled ultrastructure (uncontrolled processing) will lead to nonuniform oxidation and penetration of oxygen along the phase boundaries producing materials with unpredictable performance.

Figure 3 shows the overall approach that the multi-investigator research program has taken. The state-of-the-art in 1977 is shown as a reference point and indicates the relative performance of ceramics achieved through traditional processing techniques where powders and ultrastructure were not controlled. From 1977 through 1979, Drs. Hench and Clark developed surface techniques and models using glass and glass-ceramics for studying surface chemistry and ultrastructure. Beginning in 1979, this project was expanded to apply these concepts to learn how to produce polycrystalline ceramics.

The impact of ultrastructural processing based on chemistry can open a new era of ceramic material leadership for the United States if Government, academia and industry will recognize this opportunity. Turbine engine hot sections are but one example. Past attempts can best be analyzed as follows. Uncontrolled raw materials chemistry and processing chemistry led to uncontrolled microstructure, glass phases, oxygen penetration of grain boundaries and interfaces, and surface aggregation of densification additives. These in turn led to reduced oxidation resistance, reduced creep resistance, and unpredictable service life.

Ceramic composites are now being preached as the panacea to accomplish what bulk ceramics have not. However, those spreading this gospel should take heed that unless the chemistry and ultrastructure of the matrices, fibers and fiber-matrix interface are analyzed and controlled early in research, the same fate will be bestowed upon U.S. endeavors in this area.

The writer foresees the same consideration of chemistry and ultrastructure underlying the successful use of electronic ceramics, particularly electro-optic materials with unique non-linear optical properties. Current electro-optic materials are inorganic single crystals which are limited in performance by their growth techniques and the sensitivity of their optical properties to ionic defect chemistry. The chemical

processing approach offers the exciting potential of overcoming the problems of phase chemistry incongruency concurrent with providing homogeneous expanded compositional ranges at the ultrastructural level. Concurrent research in new quantitative, self-consistent defect chemistry models will interface here to predict new processing conditions for improved materials and devices.

Ultrastructure processing will impact the future of space, which lies in large precision space structures. The driving forces for structures are lightweight, dimensional stability, and environmental resistance. In this case, load-bearing capability is not a primary design parameter. Ultrastructure processed ceramics with tailored porosity, reinforced or unreinforced, are a viable structural option here when the problems of fiber-reinforced polymeric and other composites are considered.

The concept of ultrastructure processing through chemistry can evolve engineering materials with performance approaching the theoretical upper limit. This has already been demonstrated with the macromolecular structure of polymers by interfacing polymer chemistry with polymer physics. The Air Force Office of Scientific Research and Air Force Wright-Aeronautical Laboratory/Materials Laboratory conducted a corporate research program to develop self-reinforced or ordered polymers. The goal was the attainment of mechanical properties and environmental resistance from polymers which are compatible with those now being obtained from fiber-reinforced composites, but without the use of fiber reinforcement.

The spinoff of this polymer research program was the development of polybenzothiazole (PBT). This polymer has extended rigid chain alignment at the ultrastructural level rather than the flexible chains of resins employed as materials in fiber reinforced composites. As a result, PBT has superior tensile strength and ultra high modulus as well as excellent thermal stability and environmental resistance in comparison with aramids, other polymers, and carbon, glass, and steel fibers.

In conclusion, the future of ceramics is dependent upon the development of an interdisciplinary philosophy between chemists and ceramists. The way - ultrastructure processing through the chemistry approach - has been shown by the work of Dr. Hench and associates in the AFOSR multi-investigator approach at the University of Florida and the organosilicon chemistry program pioneered some years ago and continued by Dr. Matuszko at AFOSR. The organometallic polymer precursor approach is among the most important chemical approaches to ceramics. Others being stressed by AFOSR are sol-gel processing, and micromorphology based processing.

## AFOSR SPONSORED RESEARCH IN MOLECULAR DYNAMICS

Major William G. Thorpe

The AFOSR program in molecular dynamics is principally concerned with understanding fundamental processes of energy transfer in gas phase reactions. This program is composed of four subareas: chemical lasers, upper atmosphere chemistry, decomposition mechanisms of energetic materials, and interactive dynamics. During 1982 the plume and wake subarea was phased out.

Current chemical lasers undergoing advanced research in the Air Force are the HF/DF laser and the Chemical Oxygen Iodine Laser (COIL). During the past year the Defense Science Board and the House Armed Services Committee have called for increased basic research into lasers operating at shorter wavelengths. This interest has led to the approval of a new initiative in short wavelength lasers to begin in FY 84. In this context, short wavelength is defined as shorter than one micron. This initiative will be a joint venture involving the Physics and Chemical and Atmospheric Sciences Directorates at AFOSR. This will represent a modest growth in this task which I hope will spur interest in new laser possibilities. I expect that new chemical laser candidates are likely to be those in which the chemical pumping species is distinct from the lasing species. Currently supported research studying energy transfer dynamics and the spectroscopy of diatomic and small polyatomic species forms the basis for this new thrust.

The atmospheric chemistry subarea has primarily been concerned with optical and chemical processes occurring in the upper atmosphere. During the coming year this area will focus on ion-molecule and ion-ion reactions involving atmospheric constituents and cluster formation.

It is the aim in the new subarea on decomposition mechanisms in energetic materials to focus attention on the decomposition (combustion) of rocket propellants and the decomposition (explosion) of conventional munitions. The principle question being asked is "Is an understanding of the chemistry and microscopic energy transfer steps important in understanding and successfully modeling these rapid chemical processes." It is clear from several conferences devoted to chemical propulsion and conventional explosion that this question is not being addressed. The approach will be to determine the spectroscopy and kinetics of species initially produced by thermally or optically induced decomposition of energetical materials. Laser based techniques will be emphasized.

The goal of the approaches in the interactive dynamics subarea is a basic understanding of the interaction of optical radiation with chemical species. It encompasses some of the most long range research and enhances the more directed efforts. An example of the work in this area is the recent work of Professor Dick Zare at Stanford concerning reagent orientation and reactivity. In this work (J. Chem. Phys., 77, 2416 (1982)), a polarized laser was used to prepare aligned  $\text{Ca}(^1P_1)$  atoms



to investigate the effect of atomic reagent approach geometry (the sense of the Ca p orbital) on reactivity. Specifically, his research group examined the reactions of  $\text{Ca}(^1\text{P}_1)$  with  $\text{HCl}$ ,  $\text{Cl}_2$  and  $\text{CCl}_4$ . They find that for the  $\text{HCl}$  reagent, the orbital alignment does not effect the total yield of excited state products but it does alter the course of the reaction. It is observed that the direction of the atomic p orbital correlates with the corresponding p or p molecular orbital of the  $\text{CaCl}$  products in the  $\text{Ca}(^1\text{P}_1) + \text{HCl}$  reactions. For  $\text{Cl}_2$ , perpendicular approach of the p orbital is favored by both channels while the  $\text{CCl}_4$  reagent displays no significant sensitivity to orbital alignment. These findings can be rationalized using an electron-jump model in which the symmetry of the reagents is preserved during a reactive encounter. In addition they have examined in detail the possibilities for optical preparation of aligned molecular reagents.

The AFOSR Molecular Dynamics and Surface Chemistry Conference was held December 1-3, 1982 at the Air Force Academy, Colorado Springs, CO. An example of the cross flow of information between Air Force laboratory scientists and university research sponsored in this program is the use of new laser multiphoton techniques in the Optical Physics Division at the Air Force Geophysics Laboratory (AFGL) which were developed at Cornell University and presented at this conference. The next meeting is planned for October 1983 at AFGL, Hanscom AFB, MA.

## CHEMICAL REACTIVITY AND SYNTHESIS IN AFOSR

Dr. Anthony J. Matuszko

In the past several Annual Reviews we have selected specific achievements to highlight from our program in Chemical Reactivity and Synthesis. This year we will present an overview of the entire program as it exists today, include some thoughts about the direction in which we have been going, and present some projections for the future.

Fifteen to twenty years ago the program covered a broad area of chemical synthesis and mechanism studies. Although the emphasis then was on the rapidly expanding area of organometallic chemistry, the philosophy was to support the best research in a broad range of synthetic chemistry, research that might not solve the Air Force problems of the day but was judged to have excellent long range potential. The broad coverage included research on novel ideas and concepts for the synthesis of new and unique systems of compounds. Because of this broad approach to basic research, the program may have appeared to be somewhat fragmented. And yet, some of this funded research in the 60's formed a solid foundation for the expanding programs of the 70's and 80's.

One area which received our early attention was organosilicon chemistry. With all the exciting new chemistry evolving in the organosilicon field during the 60's and early 70's, we continued to support basic research in the area despite occasional criticism from our more practical minded friends who felt that nothing useful would come out of this work. Among the university scientists, Professor Robert West of the University of Wisconsin has been in the AFOSR Chemistry Program for over twenty years; Professor Dietmar Seyferth of MIT and Professor William Weber of the University of Southern California have received AFOSR support for ten years or more. More recent additions to the program have been Professor Philip Boudjouk of North Dakota State University and Professor Michael Jung of UCLA. Our continued support of the individuals mentioned together with our expansion in the area was due to the many new scientific discoveries coming out of the organosilicon research program and the expanding practical interest in the area. To illustrate this, Figure 1 shows a chart that I have used in recent program reviews.

One discovery that was a catalyst for our expanded interest in organosilicon chemistry was the conversion, through pyrolysis, of polyorganosilanes to high strength silicon carbide (SiC) fibers. Although the discovery was made by the Japanese, much of the research on the starting materials was done under AFOSR grants at the University of Wisconsin with Professor West and his research group. Upon returning from a lecture tour in Japan in the spring of 1976, West wrote to me about the Japanese SiC work. He was encouraged to expand his organosilicon research program to include added work on investigating the chemistry of new and better silane precursors for SiC fibers and matrix materials. A

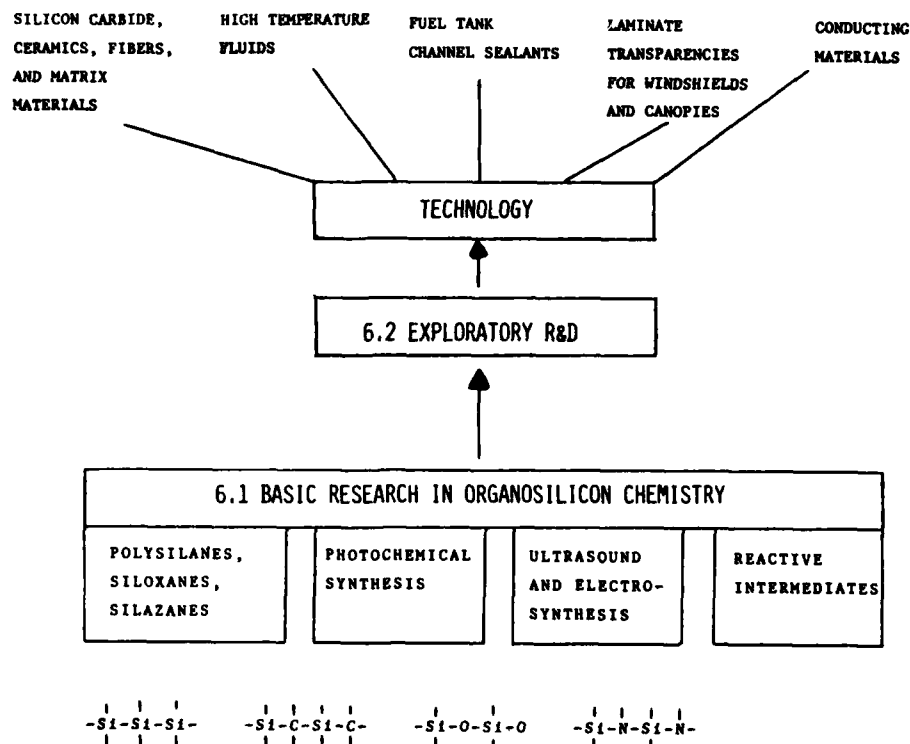


Figure 1

cooperative effort was initiated with the Air Force Materials Laboratory to test some of West's polysilane polymers in ceramics. (The cover of the 1977 AFOSR Chemistry Program Review shows a scanning electron micrograph picture of one of West's polymers after being decomposed to whiskers of  $\beta$ -SiC.) This was followed by cooperative efforts between Professor West and Professor Larry Hench of the Department of Materials Science at the University of Florida, who was receiving support under Dr. Donald Ulrich's AFOSR Structural Chemistry Program. This is one of several very fruitful interactions between organosilicon chemistry researchers and materials scientists in the AFOSR program. At a recent International Conference organized by Professor Hench and Dr. Ulrich on Ultrastructure Processing of Ceramics, Glasses and Composites, Professor West, Professor Seyferth and Professor Weber gave Science Keynote presentations on their organosilicon chemistry research for AFOSR.

Before I leave the organosilicon research program, I should like to mention two of the many important scientific discoveries in the area which evolved during our sponsorship. One occurred over ten years ago and was the first synthesis and characterization of a cyclopropylsilane by Professor Seyferth at MIT. The second which was of major scientific significance occurred in the past year when Professor West, together with Professor Michl of the University of Utah, reported the first synthesis and isolation of a silicon to silicon double bonded compound. (An X-ray

crystallographic representation of the disilene is shown on the cover.) This discovery has received extensive coverage in the scientific and news media so I won't go into any further detail in this overall summary.

A second programmatic area in which we have several research efforts is fluorine chemistry. Once again a recent briefing chart (Figure 2) summarizes the scientific areas covered and technological implication for the Air Force.

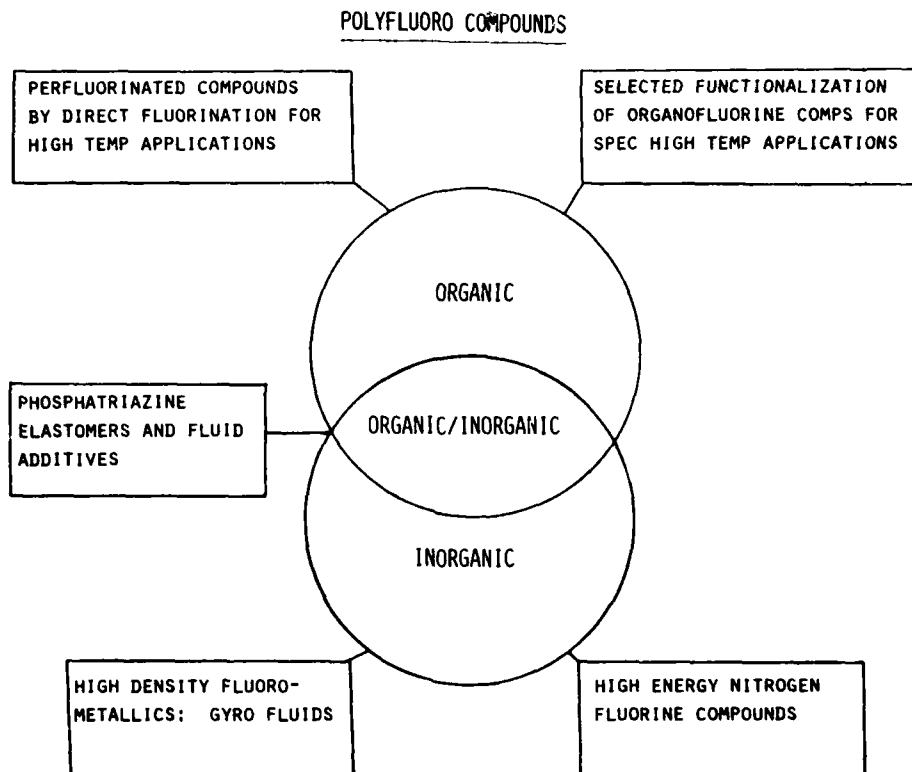


Figure 2

I discussed our program in organofluorine chemistry, including the phosphatriazine work, in last year's review. In the inorganic area, research done by Drs. Schack and Christie of Rocketdyne included the discovery of a new method for the synthesis of hypofluorites utilizing fluorine fluorosulfate as the fluorinating agent, and the first synthesis of  $\text{TeF}_5\text{OF}$ , a potential high density fluid. In an effort recently started at the University of Idaho, Professor Jean'ne Shreeve is investigating the synthesis and chemical reactivity of compounds containing nitrogen-fluorine bonds as potential high energy propellant compounds.

In addition to the two programmatic areas mentioned, we have research in three AFOSR multidisciplinary "New Initiatives" programs. In Defense Against Chemical Agents, we have work on molecular orbital approaches to studying the properties and reactivity of chemical agents. In an

initiative on Spacecraft Propulsion, we have research into the synthesis of new high energy compounds. And in the Spacecraft Structures and Materials initiative, we have work additional to our core research programs in organosilicon chemistry.

Finally, a portion of the core program support in Chemical Reactivity and Synthesis (approximately 25 to 30%) is reserved for new ideas and new concepts not related to the larger programmatic areas mentioned above. Some of these are funded for only a three or four year period. Others have been going for longer periods of time. I will just mention a few of these research efforts. One such program which has been highly productive for several years is that of Professor Michael Dewar at the University of Texas on the development of methods for semi-empirical molecular orbital calculations. There have been collaborative efforts between Dewar and scientists from the F. J. Seiler Research Laboratory in Colorado Springs applying Dewar's MINDO and MNDO approaches to Air Force research problems, particularly those applied to explosives and propellants. At Columbia University, Professors Turro and Eisenthal have been studying photochemical reactions of organic compounds and mechanisms of fast reactions in solution with picosecond spectroscopy. Dr. Philip Skell at Pennsylvania State University has over the years studied carbon atom chemistry and pioneered methods of studying the chemistry and reactivity of metal atoms. Dr. Marge Nicholson at Rockwell International has done some really nice work on determining mechanisms and rate parameters for electrochromic transformations in rare earth diphthalocyanine complexes.

Future directions for the program are difficult to predict. For the immediate future we plan to continue a concentrated effort in organosilicon chemistry since we feel this is an area that has a great deal of potential. Because of our limited funding, new work will have to be really innovative. We plan to continue, but not expand, a program in fluorine chemistry. And finally, we will consider any exciting new ideas related to synthesis, particularly in the organometallic or organometalloid area.

## ATMOSPHERIC SCIENCES

Lieutenant Colonel Ted S. Cress

Major James E. Metcalf  
(USAF Reserve)

As the "single manager" for the Air Force basic research program, AFOSR supports atmospheric research through an extramural research program as well as an in-house research program at AF laboratories. While AFOSR maintains an active extramural program, the overall atmospheric sciences basic research program is dominated by the in-house and contractual programs at the Air Force Geophysics Laboratory (AFGL). In contrast to the AFGL basic research program which supports the exploratory development efforts at the laboratory, the AFOSR sponsored extramural program is more widely ranging, more high risk, and looks towards the fundamental knowledge that will serve problem solving efforts in the future. Close coordination between efforts at AFOSR and AFGL insures complementary programs and avoidance of duplicative efforts.

The purpose of the AFOSR atmospheric sciences basic research program is to stimulate and support innovative research that will ultimately lead to a more thorough understanding of the fundamental physical processes of the atmosphere. The range and scope of the program addresses phenomena across the spectrum from molecular to global, from the earth's surface to the atmosphere's outer limits. This domain includes nearly all of the geophysical processes influencing the use and performance of current and proposed Air Force systems including space-based communications and surveillance. Environmental effects on space-based systems, e.g., drag and surface chemistry, are generally covered under other AFOSR program areas. Magnetospheric processes are addressed within this program where ionospheric behavior must be understood.

The Atmospheric Sciences program is structured into two classical research areas; meteorology, and the upper atmosphere. Within these general categories, areas of emphasis are imbedded and enjoy the greater share of available funding. In FY 82, maintaining recent directions, the meteorology program emphasized three areas; mesoscale meteorology, cloud physics, and atmospheric dynamics. In the upper atmosphere, efforts were focused on a large cooperative effort to understand the global character of auroral zone variability.

The goal of this short descriptive effort will be to address the major research areas, describe recent developments, emphasize foci of interest, and speculate on the future course of the sponsored program. The philosophy of concentration of effort in the research program will be apparent in this description. It is hoped this philosophy will avoid a "scatter-gun" approach and will lead to major new advances beyond those which would be produced by research efforts proceeding in "splendid isolation." The most rapid advance of scientific knowledge and understanding hinges on communication and the existence of a "critical mass." We strive for both.

## Meteorology

The current program in meteorology is reflective of deliberate focusing. Mesoscale dynamics continues to be the the core focus; interdependent processes such as convection, radiation, and energy exchange with the planetary boundary layer (PBL) are key subinterests. Two related fields of research round out the current program; these include cloud physics and an exciting new capability to study vertical coupling and energy exchange processes - VHF radar. As a general statement, these topic areas will remain areas of concern and emphasis for the foreseeable future.

Other areas of potential interest are many, but several of the more critical areas are aerosol physics, optical/IR transmission characteristics of clouds (i.e., the morphology of the hydrometeor populations), and the dynamics of the planetary boundary layer.

Among the specific research efforts in mesoscale meteorology are those of Drs. Toby Carlson, Tom Warner and Mike Fritsch at Pennsylvania State University and Dr. Elmar Reiter at Colorado State University. The Pennsylvania State group has been conducting simulation modeling using the Anthes-Warner model to investigate large scale forcing of mesoscale developments and the sensitivity of mesoscale development to planetary boundary layer (PBL) coupling and interaction with topography. From the modeling aspect, the current emphasis is to investigate the importance of high-resolution boundary layer parameterizations and the role of horizontally variable parameters such as moisture and surface heating. Dr. Reiter is examining the role of elevated terrain in the initiation and development of mesoscale convective weather systems; the focus of his effort lies in the surface energy budget of high terrain and the horizontal transport of atmospheric moisture. Based on data availability, the two primary areas of interest for this effort are the Tibetan Plateaus and the Southwest United States.

With respect to the future, it is fair to assume that mesoscale meteorology will remain a major part of the AFOSR program. Mesoscale weather has always been recognized as a major area of interest to DOD (e.g., battlefield weather) and has been a key focus area for several years. With the planning for, and advent of, the National "STORM" Program (outlined recently by a UCAR study), AFOSR will remain deeply interested in mesoscale research and will, in all probability, sponsor research efforts in support of, or complementary to, the national effort.

In cloud physics, the center of activity continues to be the tri-service sponsored effort by Dr. James Kassner, University of Missouri-Rolla, to build a cloud simulation chamber of unsurpassed capability. At the current time the so-called "ROMULUS" chamber is being assembled and is anticipated to be operational in January 1984. It is anticipated that the future cloud physics program will revolve about the capabilities of this chamber for cloud, aerosol and optical physics research. In another cloud physics effort, Dr. David Johnson at the Illinois Water Survey is looking at the microphysical mechanisms of precipitation. In the first year of this effort, Dr. Johnson has produced modeling results that show that

droplet size and liquid water content are simultaneously important in the initiation of the coalescence process and, as such, are directly related to cloud base temperature, e.g., he finds that warm based clouds can experience effective coalescence growth even in regions characterized by average water contents, but that in cold based clouds, average water contents would not be adequate to support effective coalescence growth. Dr. Johnson's effort in the future will include studies of the ice multiplication process and additional warm cloud precipitation modeling.

In studying vertical coupling and energy transport, the mesospheric-tropospheric-stratospheric (MST) VHF radar developed by NOAA continues as an exciting new research tool. AFOSR is continuing to sponsor several studies of lower atmospheric dynamics with this facility and in the future may sponsor further investigations of vertical dynamic coupling. This radar's utility for synoptic or mesoscale research is intriguing and its potential for operational application is promising. Support to conduct quantitative investigations of atmospheric synoptic features is likely.

#### Upper Atmosphere

The upper atmosphere research program is currently focussed on understanding the temporal and spacial morphology of ionospheric structure (specifically electron density irregularities and gradients) and the dynamics of upper atmospheric motion. These questions are global in nature and impact numerous research areas such as auroral zone phenomenology, equatorial F-region irregularities, neutral winds, chemical species distribution, solar impacts on the neutral atmosphere, temporal and spacial ionospheric disturbances, inadvertent and planned ionospheric modification and ionospheric-magnetospheric coupling (modeling).

Current funding is strongly directed toward the spacial and temporal variability of the auroral zone ionosphere and the morphology of electron density irregularities at high latitudes. Smaller efforts address the spectrum of scintillation-causing electron density irregularities and the role of neutral atmospheric processes in the global distribution of middle (10-100 km) atmospheric trace species.

The core effort of the upper atmosphere program at this time is a joint agency, international, multiple investigator research effort known by the acronym, MITHRAS. The purpose of this project is to study in detail the high latitude upper atmosphere (ionosphere and thermosphere). This effort includes field measurements and analysis as well as theoretical modeling. The critical measurement facilities (May 1981 through June 1982) were three incoherent scatter radar systems widely spaced (longitudinally) around the auroral zone: Chatanika (Alaska), Millstone Hill (Massachusetts), and EISCAT (Scandinavia). Other measurements being included in the analysis are data from the NASA DE satellites, the Scandinavian Twin Auroral Radar Experiment (STARE), and the worldwide magnetometer network. The principal participants are the research groups at SRI International and MIT. Other investigators include groups at Utah State University, the University of Texas-Dallas, Stanford University, the National Center for Atmospheric Research (NCAR) and NOAA.



Internationally, major contributions are being made by the French Incoherent Scatter group at the Centre National D'Etudes de Telecommunications (CNET), and by the EISCAT (European Incoherent Scatter Research Association) community without whose cooperation this effort could not have been undertaken. EISCAT is supported by the Suomen Akatemia (Finland), the Centre National de la Recherche Scientifique (France), the Max-Planck Gesellschaft (West Germany), the Norges Almenvitenskaplige Forskningsrod (Norway), the Naturvetenskapliga Forskningsrodet (Sweden), and the Science Research Council (UK). The experiments and analysis of this effort were motivated by the need to better understand the coupling between the magnetosphere, the ionosphere and the thermosphere; this is a dynamic system of considerable complexity which has, so far, frustrated efforts to fully describe the coupling mechanisms. A proper combination of detailed and complete observations, together with theoretical modeling is necessary to further knowledge of these processes; specifically, a simultaneous measurements program looking at large sections of the auroral zone was considered necessary to resolve many of the ambiguities between local time and universal time dependencies that resulted from a long history of single site experimental efforts. Specific topics being addressed include ion convection, discrete and diffuse aurorae, the midlatitude trough, field-aligned currents, and neutral winds. The initial SRI contract to acquire the data and begin the analysis effort is being concluded in FY 83 and will be summarized in this publication next year. A number of follow-on analytical efforts are being supported by AFOSR and NSF. It is anticipated that these analytical and modeling studies will be completed over the next few years.

#### Planning the Future in Upper Atmosphere Research

Planning the AFOSR research program is an ongoing activity: results of investigations underway are incorporated as they become known, research interests of current or prospective grantees and the availability of various types of research data from specialized sensors are weighed, and the evolving needs of the Air Force are assessed. The continuing development of upper atmospheric sensing equipment and the need for multiple-sensor observations to study the global characteristics of the upper atmosphere are two factors strongly influencing the future directions of the AFOSR research program. Considering the development of research areas on a long time scale, i.e., ten years or more, is necessary to guide the overall program which evolves through the efforts of grantees on a year-to-year basis. In the current program several emphases are discernible and serve as the starting point for the future program. One emphasis is on the small-scale structure of ionospheric irregularities as observed by incoherent-scatter radars and by satellite beacon scintillation measurements. Another is the joint interpretation of data from coordinated observations such as the MITHRAS Program discussed above. In such coordinated efforts some, but not necessarily all, of the participants are AFOSR grantees.

Emphasis will continue on the measurement, interpretation, and modeling of small-scale ionospheric structures, e.g., scales of tens of kilometers or less, using satellite beacon scintillation, incoherent-scatter radar and

Dynamics Explorer satellite data and other new data such as may be forthcoming from the DNA polar satellite scheduled for launch in mid-1983, and from chemical release experiments. One example of a phenomenon requiring detailed study are the "sub-visual F-region arcs," bands of enhanced ionization oriented in the solar-anti-solar direction and moving transverse to that direction, which were first observed by AFGL in January 1982.

The recently completed move of the Chatanika incoherent scatter radar to Sondre Stromfjord, Greenland, provides a new capability for observing ionospheric structure in the polar cap and also completes a line of incoherent scatter radars extending to Jicamarca, Peru, on the magnetic equator. In addition to the new opportunities for studies of the polar cap structure at various scales, the array of radars permits observations of full latitudinal variations of ionospheric structure. The observational capability should permit the study of interactions of ionized and neutral components of the atmosphere, the meridional transport of energy in response to inputs in the auroral and polar regions, and the propagation of ionospheric disturbances. AFGL is planning studies of this type to be conducted during the next four years. AFOSR contemplates the support of related studies during a comparable or somewhat longer time period.

The understanding of global characteristics of the ionosphere involves the interactions between or among various components and altitude regions. One area of particular interest is the vicinity of the mesopause, near 90 km altitude. Study of this region has always been difficult, due to deficiencies of observational techniques. Balloons cannot reach this altitude, sounding rockets are typically moving too fast in passing this altitude, incoherent scatter radars have limited capability below about 100 km, and radars detecting back-scatter from fluctuations of microwave refractive index (the "mesosphere-stratosphere-troposphere (MST)" radars) have reduced nighttime capability above about 50 km and have an effective maximum range near 100 km. In summary, there is limited measurement capability spanning the altitude range from 80 to 120 km, from the upper mesosphere to the lower thermosphere. The microwave limb sounder developed by Jet Propulsion Laboratory offers a new opportunity to observe key atmospheric parameters in this region; the sounder is to be flown on the NASA Upper Atmosphere Research Satellite (UARS), originally conceived to be part of the Middle Atmosphere Program but now rescheduled for launch about 1988. The new sensing capabilities represented by UARS and by the NASA Origin of Plasmas in the Earth's Neighborhood (OPEN) program will provide a data base for experimental and modeling studies of the neutral and ionized upper atmosphere extending well into the future. Some studies now being supported by AFOSR aim at understanding physical and chemical processes of the upper atmosphere through simulation models. The continuation of this type of research, incorporating experimental data where possible, will effectively prepare for the optimum use of data from the coming satellite-based sensors.

The preceding discussion of potential future research interests, while neither inclusive nor exclusive, is intended to illustrate the

considerations that guide the development of the AFOSR program. The fundamental goal of all the atmospheric research sponsored by AFOSR is the increased understanding of the dynamical, physical, and chemical processes through which the atmosphere evolves. The results of the research may be expected to improve understanding of the environment in which aerospace systems operate and of the effects of AF operations on the environment.

RESEARCH EFFORTS COMPLETED IN FY82

CHEMICAL TECHNIQUES - DENTON W. ELLIOTT

Fundamental Studies of Under-  
potential Metal Deposition and  
Trace Analysis Using Solid  
Electrodes  
AFOSR-78-3621

Stanley Bruckenstein  
Department of Chemistry  
State Univ. of New York at Buffalo  
Buffalo, NY 14214

New Materials for  
Electrochemical Cells  
AFOSR-77-3402

John B. Goodenough  
Peter G. Dickens  
Inorganic Chemistry Laboratory  
University of Oxford  
Oxford, England OX1 3QR

Secondary Ion Mass Spectroscopic  
Studies of Electrode Surfaces  
AFOSR-80-0002

Nicholas Winograd  
Department of Chemistry  
Pennsylvania State University  
University Park, PA 16802

## COMPLETED PROJECT SUMMARY

1. TITLE: Fundamental Studies of Underpotential Metal Deposition and Trace Analysis Using Solid Electrodes

2. PRINCIPAL INVESTIGATOR: Dr. Stanley Bruckenstein  
Department of Chemistry  
State University of New York at Buffalo  
Buffalo, NY 14214

3. INCLUSIVE DATES: 15 May 1978 - 30 September 1982

4. GRANT NUMBER: AFOSR-78-3621

5. COSTS AND FY SOURCE: \$59,442, FY79; \$111,980, FY80; \$86,809, FY81;  
\$90,468, FY82

6. SENIOR RESEARCH PERSONNEL:

Dr. P. Beran  
Dr. Y. Kanzaki  
Dr. S. Swathirajan

Dr. K. S. Chung  
Dr. H. Mizota  
Dr. K. Tokuda

7. JUNIOR RESEARCH PERSONNEL:

P. Gifford  
R. F. Mack  
L. S. Melnicki  
K. A. Tucker

J. D. Jolson  
G. A. Martincheck  
J. S. Symanski

8. PUBLICATIONS:

"Isotherm and Electroadsorption Valency For Underpotential Deposits of Silver on Gold," T. Riedhammer, L. S. Melnicki and S. Bruckenstein, Z. Phys. Chem., N.F. 111, 177 (1978).

"Sinusoidal Hydrodynamic Voltammetry. I. Theory of Electron Transfer Processes," K. Tokuda and S. Bruckenstein, J. Electrochem. Soc., 126, 431 (1979).

"Sinusoidal Hydrodynamic Voltammetry. II. Experimental Test of the Electron Transfer Theory," Y. Kanzaki and S. Bruckenstein, J. Electrochem. Soc., 126, 437 (1979).

"A Closed Form Expression for the Primary Resistance at a Ring Electrode," S. Bruckenstein and G. Martincheck, J. Electrochem. Soc., 126, 1307 (1979).

"Micromolar Voltammetric Analysis by Ring Shielding at a Rotating-Ring Disk Electrode," S. Bruckenstein and P. Gifford, Anal. Chem., 51, 250 (1979).

"Hydrodynamic Modulation at a Rotating Disk Electrode," W. J. Albery, A. R. Hillman and S. Bruckenstein, J. Electroanal. Chem., 100, 687 (1979).

"Studies of Underpotential Silver on Platinum and Gold," L. S. Melnicki, T. M. Riedhammer and S. Bruckenstein, Proceedings of the Third Symposium on Electrode Kinetics, 1979. S. Bruckenstein, B. Miller, J.E.D. McIntyre and E. Yeager, Eds., Proceedings Volume 80-3, The Electrochemistry Society, Inc., 306 (1980).

"Rotating Disk Electrode Studies of Formation, Growth and Transformation of Iodine Films During the Anodic Oxidation of Iodide on Platinum," S. Swathirajan and S. Bruckenstein, J. Electroanal. Chem., 112, 25 (1980).

"Pneumatoamperometric Determination of Parts-per-Billion Dissolved Species Using Gas Evolving Reactions," P. Gifford and S. Bruckenstein, Anal. Chem., 52, 1024 (1980).

"Separation and Determination of Volatile Hydrides by Gas Chromatography Using a Gold Gas Porous Electrode," P. Gifford and S. Bruckenstein, Anal. Chem., 52, 1028 (1980).

"Pneumatoamperometric Determination of Nanogram Amounts of Cyanide," P. Beran and S. Bruckenstein, Anal. Chem., 52, 1183 (1980).

"Theory of the Pneumatoamperometric Method," P. Beran and S. Bruckenstein, Anal. Chem., 51, 2207 (1980).

"Determination of Sulfur Dioxide by Reaction with Electrogenerated Bromine in a Thin-Layer Cell Having a Gas-Porous Wall," S. Bruckenstein, K. A. Tucker and P. R. Gifford, Anal. Chem., 52, 2396 (1980).

"Pneumatoamperometric Determinations of Various Oxidants and Total Dissolved Chlorine," Premysl Beran and Stanley Bruckenstein, Analytical Chemica Acta, 136, 389 (1982).

"Pneumatoamperometric Determinations of Sub-PPM Amounts of Ruthenate and Osmate," P. Beran, K. S. Chung and S. Bruckenstein, Talanta, in press.

"Ring-Disk Electrode Studies of the Open-Circuit Dissolution of Iodine Films Formed During the Anodic Oxidation of Iodide on Platinum," S. Swathirajan and S. Bruckenstein, J. Electroanal. Chem., 125, 63 (1981).

"Interpretation of Potentiostatic Transient Behavior During the Underpotential Deposition of Silver on Gold using the Rotating Ring Disk Electrode," S. Swathirajan and S. Bruckenstein, J. Electrochem. Soc., 129, 1202 (1982).

"Current-Voltage Analysis of Photoelectrochemical Cells under Mass and Light Flux Variation," S. Bruckenstein and B. Miller, Symposium Volume on Measurement Techniques for Photoelectrochemical Solar Cells, 160th Meeting of the Electrochemical Society, Denver, Colorado, 11-16 October 1981, in press.

"Thermodynamic Properties of Monolayer of Silver and Lead Deposited on Polycrystalline Gold in the Underpotential Region," S. Swathirajan, H. Mizota and S. Bruckenstein, J. Phys. Chem., 86, 2480 (1982).

"Current-Voltage Analysis of Photoelectrochemical Cells Under Mass and Light Flux Variation," S. Bruckenstein and B. Miller, J. Electrochem. Soc., 129, 2029 (1982).

"The Anodic Behavior of Iodide at Platinum in the Presence of an Iodine Film Under Potentiostatic Steady-State and Hydrodynamic Modulation Conditions," S. Swathirajan and S. Bruckenstein, J. Electroanal. Chem., in press.

"Uniformly Accessible Electrodes," W. John Albery and S. Bruckenstein, J. Electroanal. Chem., in press.

"Interpretation of the Potentiodynamic Response during the Underpotential Deposition of Silver on Polycrystalline Gold," S. Swathirajan and S. Bruckenstein, J. Electroanal. Chem., in press.

"Thermodynamics and Kinetics of Underpotential Deposition of Metal Monolayers on Polycrystalline Substrates," S. Swathirajan and S. Bruckenstein, Electrochimica Acta, in press.

"Conductometric Sensor for Atmospheric Carbon Dioxide Determination," J. S. Symanski, G. A. Martincheck and S. Bruckenstein, Anal. Chem., in press.

"Ad-Atom Coverage Studies During the Catalysis and Inhibition of Formic Acid Electrooxidation by Underpotential Deposition," Mani Shabrang, H. Mizota and S. Bruckenstein, J. Electrochem. Soc., submitted.

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

One of the objectives of this research was to study and to interpret the behavior of films at solid electrodes. With a sound understanding of the characteristics of submonolayer, monolayer and thicker films and their effect on electrochemical processes, it should be possible to apply this knowledge to understanding important solution heterogeneous processes, such as corrosion and electrocatalysis (by underpotential metal deposition). A second objective was to develop new approaches to studying electrochemical reactions at solid electrodes, particularly the use of controlled hydrodynamics, in order to provide new diagnostic criteria for elucidating complex electrode processes. Another goal was to apply solid electrode structures to analytically important problems.

Experimental and theoretical underpotential metal deposition studies at polycrystalline gold and platinum have led to a thermodynamic interpretation of the isotherm for the underpotential deposition (UPD) of lead and silver. The relationships between the underpotential, work function, point of zero charge, and coverage have been obtained in the absence of specific adsorption. Preliminary studies of the change of

point of zero charge with underpotential coverage of silver on gold confirm the theoretical predictions, and demonstrate that there is a double layer charging current that accompanies the change in point of zero charge with change of UPD coverage. The thermodynamics and kinetics of the underpotential deposition of silver on gold have been successfully interpreted using the isotherm and ring shielding currents obtained at a rotating ring-disk electrode to separate the double layer charging currents from the instantaneous flux of UPD species at the disk electrode.

A study of the electrocatalysis of the oxidation of formic acid oxidation by the UPD of lead, bismuth of thallium on polycrystalline platinum has shown that the third body hypothesis is a satisfactory explanation. It is necessary, however, to take into account the selective UPD of these metals and the uncatalyzed oxidation process on the various crystal planes of platinum. The lack of catalysis of the formic acid oxidation process by UPD silver and copper has been shown to be caused by the selective UDP of these metals on the platinum plane which contributes least to the uncatalyzed oxidation process.

The theory of hydrodynamic modulation at a rotating disk electrode was extended to the electron transfer and preceding homogeneous reaction cases. Use was made of the experimental technique in our UPD and thick film studies. In particular, the formation of thick iodine films on platinum was demonstrated to be totally under mass transfer control. The ultimate thickness of the film can be described in terms of reversible electrode potential for the iodine/iodide couple, the triiodide equilibrium and diffusion of iodide ion through the iodine film. Hydrodynamic modulation was also applied to the interpretation of the current-potential response of photoelectrochemical cells having "pinned junctions". The approach outlined can, in principle, be used for illuminated, unpinned semiconductor/electrolyte interfaces.

The analytical application of porous electrode structures to trace analysis of aqueous solutions lead to the development of pneumatoamperometric method. In this method a volatile, electroactive solute present in solution is purged from solution using a nonelectroactive gas and the gas stream impinged on the gas phase side of a porous electrode held at potential to electrolyze the electroactive species. If the solute is not volatile, a suitable chemical reaction is carried out to produce a volatile species. This technique has been demonstrated to have anogram sensitivity, and has been used to determine iodide, iodate, cyanide, arsenic, antimony, tin, osmium, rhuthenium and a wide variety of oxidizing agents.

AFOSR Program Manager: Denton W. Elliott



## COMPLETED PROJECT SUMMARY

1. TITLE: New Materials for Electrochemical Cells
2. PRINCIPAL INVESTIGATORS: Professor John B. Goodenough  
Dr. Peter G. Dickens  
Inorganic Chemistry Laboratory  
University of Oxford  
Oxford OX1 3QR  
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3. INCLUSIVE DATES: 1 January 1978 - 31 December 1981
4. GRANT NUMBER: AFOSR-77-3402
5. COSTS AND FY SOURCE: \$23,640, FY78; \$32,128, FY79; \$30,000, FY80;  
\$32,580, FY81
6. SENIOR RESEARCH PERSONNEL:

K. Mizushima	O. Nakamura
Dr. R. C. T. Slade	T. Takeda
Dr. P. J. Wiseman	
7. JUNIOR RESEARCH PERSONNEL:

D. P. Birkett	J. J. Birtill
M. F. Cross	W. H. England
S. J. French	S. J. Hibble
A. T. Hight	R. H. Jarman
M. F. Pye	F. J. Reynolds
8. PUBLICATIONS:

"Hydrogen Molybdenum Bronzes," P. G. Dickens and J. J. Birtill, J. Elec Mater., **7**, 679 (1978).

"Elastic and Inelastic Neutron Studies of Hydrogen Molybdenum Bronzes," P. G. Dickens, J. J. Birtill and C. J. Wright, J. Solid State Chem., **28**, 185 (1979).

"Thermochemistry of Hydrogen Molybdenum Bronze Phases  $H_xMoO_3$ ," J. J. Birtill and P. G. Dickens, J. Solid State Chemistry, **29**, 367 (1979).

"NMR Study of Hydrogen Molybdenum Bronzes:  $H_{1.7}MoO_3$  and  $H_{0.36}MoO_3$ ," R.C.T. Slade, T. K. Halstead and P. G. Dickens, J. Solid State Chem., **34**, 183 (1980).

"Some Insertion Compounds of Molybdenum Trioxide," J. J. Birtill and P. G. Dickens, Extended Abstracts, Second International Meeting on Solid Electrolytes, St. Andrews, Scotland (1978).

"NMR Study of Hydrogen Molybdenum Bronzes,  $H_{1.7}MoO_3$  and  $H_{0.36}MoO_3$ ," P. G. Dickens, F. K. Halstead and R.C.T. Slade, J. Solid State Chem., **34**, 183-192 (1980).

"NMR Study of Water Reorientation in Molybdic Acids:  $MoO_3 \cdot 2H_2O$  and Yellow  $MoO_3 \cdot H_2O$ ," R. H. Jarman, P. G. Dickens and R.C.T. Slade, J. Solid State Chem., **39**, 387 (1981).

"Phase Relationships in Ambient Temperature  $Li_xV_2O_5$  System ( $0.1 < x < 1.0$ )," P. G. Dickens, S. J. French, A. T. Hight and M. F. Pye, Mat. Res. Bull., **14**, 1295 (1979).

"Thermochemistry of the High and Ambient Temperature Lithium Vanadium Bronzes  $Li_xV_2O_5$ ," P. G. Dickens, S. J. French, A. T. Hight, M. F. Pye and G. J. Reynolds, Solid State Ionics, **2**, 27 (1981).

"Ion Insertion at a Vanadium Pentoxide Cathode," P. G. Dickens, S. J. Hibble and R. H. Jarman, Extended Abstract, J. Electrochemical Society Montreal Meeting 1982, in press.

"Hydrogen Insertion Compounds of Transition Metal Oxides," P. G. Dickens, S. J. Hibble and R. H. Jarman, J. Electronic Material, **10**, 999 (1981).

"Transport and Equilibrium Properties of Some Oxide Insertion Compounds," P. G. Dickens and G. J. Reynolds, Proc. Int. Conf. on Fast Ionic Transport in Solids, Gatlinburg Penn, 18-22 May 81, B. C. Farrington and S. B. Bates, Eds. (North Holland, in press).

"Transport and Equilibrium Properties of Some Oxide Insertion Compounds," P. G. Dickens and G. J. Reynolds, Solid State Ionics, **5**, 331 (1981).

"Electrochemical Insertion of Hydrogen in  $WO_3$ ," R. H. Jarman and P. G. Dickens, J. Electrochem Soc., in press.

"Thermochemistry of Lithium Molybdenum Ternary Oxide Phases,  $Li_xMoO_3$ ," P. G. Dickens and G. J. Reynolds, in press.

"Electrochromism in Solid Phosphotungstic Acid," P. G. Dickens and R. H. Jarman, J. Electrochem Soc., **128**, 1390 (1981).

"Fast Proton Conduction in Inorganic Ion-Exchange Compounds," W. A. England, M. G. Cross, A. Hamnett, P. J. Wiseman and J. B. Goodenough, Solid State Ionics, **1**, 231 (1980).

"A.C. Proton Conduction in Hydrated Oxides," D. J. Dzimitrowicz, J. B. Goodenough and P. J. Wiseman, Mat. Res. Bull., in press.

" $Li_xCoO_2$  ( $0 < x \leq 1$ ): A New Energy Density Battery Cathode Material," K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, Mat. Res. Bull., **15**, 783 (1980).

"Solid-Solution Oxide for Storage-Battery Electrodes," J. B. Goodenough, K. Mizushima and T. Takeda, Jap. J. Appl. Phys., **19**, Supplement 19-3, 305 (1981).

"Fast Lithium Ion Transport in Composites Containing Lithium-Bromide Dihydrate," O. Nakamura and J. B. Goodenough, Solid State Ionics (in press).

"Conductivity Enhancement of Lithium Bromide Monohydrate by  $\text{Al}_2\text{O}_3$  Particles," O. Nakamura and J. B. Goodenough, Solid State Ionics, in press.

"Crystal Chemistry of the  $(\text{Ta}_6\text{Si}_4\text{O}_{26})^{6-}$  and  $(\text{Ta}_{14}\text{Si}_4\text{O}_{47})^{8-}$  Frameworks," D. P. Birkett, P. J. Wiseman and J. B. Goodenough, J. Solid State Chem. **37**, 6 (1981).

#### 9. PATENTS:

"New Fast Ion Conductors," J. B. Goodenough, K. Mizushima, and P. J. Wiseman, U.S. Patent Number 06/135222 (1980).

"New Solid Proton Conductors," M. G. Cross, D. J. Dzimitrowicz, W. A. England and P. J. Wiseman, N.R.D.C. Provisional Patent (1980).

"Synthetic Procedure for High Area Oxide Cathodes," K. Mizushima and P. J. Wiseman, A.E.R.E. Harwell Provisional Patent (1980).

#### 10. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The research had two main aims: (i) determination of the thermochemical, structural, and basic electrochemical properties of mixed electronic/ionic conductors and (ii) design, preparation and characterization of new ionic conductors, both electronic insulators for electrolytes and electronic conductors for battery cathodes and display.

The first objective was successfully carried out on the hydrogen molybdenum bronzes  $\text{H}_x\text{MoO}_3$ , the system  $\text{Li}_x\text{V}_2\text{O}_5$ , the hydrogen tungsten bronzes  $\text{H}_x\text{WO}_3$ , and the system  $\text{Li}_x\text{MoO}_3$ . This work was supplemented by NMR studies on hydrates.

Work toward the second objective also concentrated on  $\text{H}^+$  ion and  $\text{Li}^+$  ion conductors. They were able to demonstrate that classical ion-exchange materials form a broad class of  $\text{H}^+$  ion conductors that can be separated into two groups; framework hydrates and particle hydrates. Moreover they showed that the best protonic conduction would be found in hydrates of highly acidic or highly basic oxides, the highest water content compatible with retaining a solid representing the optimum condition. They also showed that particle hydrates can be formed into dense ceramics of large surface area by cold pressing, and that under a controlled  $\text{H}_2\text{O}$  atmosphere the ceramic remains solid and retains its water to nearly  $100^\circ\text{C}$ . The best  $\text{H}^+$  ion conductor was antimonitic acid, a framework hydrate, that was fabricated as a particle hydrate and cold pressed to  $\text{Sb}_2\text{O}_5 \cdot 5.4\text{H}_2\text{O}$ . At room temperature, the  $\text{H}^+$  ion conductivity approached  $10^{-2} \text{ ohm}^{-1}\text{cm}^{-1}$ .

They also demonstrated that important new materials can be fabricated by low-temperature techniques, including room-temperature electrochemistry. The first exploitation was the preparation of the systems  $\text{Li}_{1-x}\text{CrO}_2$ ,  $\text{Li}_{1-x}\text{CoO}_2$  and  $\text{Li}_{1-x}\text{NiO}_2$ . Most work has been done on the latter two systems, which give over 4V when used as a cathode against elemental lithium as the anodes. Work on the system  $\text{Na}_{1-x}\text{CoO}_2$  proved that  $\text{Na}^+$  ions have a preference for trigonal prismatic sites that reduces the solid-solution range. For the Lithium systems that range is  $0 \leq x \leq 1$ .

They also concluded that the best composite electrodes will consist of a molten salt that is immobilized by a porous (pressed-particles) insertion-compound electrode; these composites may need to be separated by a solid electrolyte.

An investigation of  $\text{LiBr} \cdot n\text{H}_2\text{O}$ ,  $1 < n < 2$ , with and without  $\text{Al}_2\text{O}_3$  particles demonstrated that molten salts can be immobilized if hydrogen-bond bridges between particles can be formed. However, they need to eliminate the water, and have begun to investigate anhydrous salts molten at room temperature.

An investigation of  $\text{Na}^+$  ion transport in a new framework structure proved disappointing.

AFOSR Program Manager: Denton W. Elliott

## COMPLETED PROJECT SUMMARY

1. TITLE: Secondary Ion Mass Spectroscopic Studies of Electrode Surfaces
2. PRINCIPAL INVESTIGATOR: Professor Nicholas Winograd  
Department of Chemistry  
Pennsylvania State University  
University Park, PA 16802
3. INCLUSIVE DATES: 1 October 1980 - 30 September 1982
4. GRANT NUMBER: AFOSR-80-0002
5. COSTS AND FY SOURCE: \$70,000, FY80; \$85,000, FY81
6. SENIOR RESEARCH PERSONNEL:

Dr. B. J. Garrison  
Dr. W. N. Delgass

### 7. PUBLICATIONS:

"Azimuthal Anisotropies of Dimer Ions Ejected from Ion Bombarded Ni(001)," S. P. Holland, B. J. Garrison and N. Winograd, Phys. Rev. Letter., **44**, 756 (1980).

"X-ray Photoelectron Spectra of Some Dirhodium Carboxylate Complexes," A. M. Dennis, R. A. Howard, K. M. Kadish, J. L. Bear, J. Brace and N. Winograd, Inorg. Chem. Acta Lett., **44**, L139 (1980).

"X-ray Photoelectron Spectroscopic Studies on Monomeric and Dimeric Iron Porphyrins," K. M. Kadish, L. A. Bottomley, J. G. Brace and N. Winograd, J. Am. Chem. Soc., **102**, 4341 (1980).

"Oxidation of Polycrystalline Indium Studies by XPS and Static SIMS," R. W. Hewitt and N. Winograd, J. Appl. Phys., **51**, 2620 (1980).

"SIMS/XPS Study of CO Chemisorption on Polycrystalline Pd, Ag, and a PdAg Alloy," G. J. Slusser and N. Winograd, Surf. Sci., **95**, 53 (1980).

"X-ray Photoemission Studies of Atom Implanted Matrices: Ni in Carbon," R. A. Gibbs, N. Winograd and V. Y. Young, J. Chem. Phys., **72**, 4799 (1980).

"Determination of Surface Structures with Ion Beams," N. Winograd, S. P. Holland, K. E. Foley, and R. A. Gibbs, Le Vide, Les Couches Minces, **201**, 427 (1980).

"Surface Structure Determinations with Ion Beams," N. Winograd and B. J. Garrison, Acc. of Chem. Res., **13**, 406 (1980).

"SIMS/XPS Study of CO Adsorption on Ni and of Fischer-Tropsch Synthesis on FeRu Alloys," T. Fleisch, N. Winograd, and W. N. Delgass, Sur. and Interf. Anal., 3, 23 (1981).

"ESCA and Electrode Surface Chemistry," J. S. Hammond and N. Winograd, in Comprehensive Treatise on Electrochemistry, Vol V, Chapter 9, J. O'M. Bockris, D. E. Conway, and E. B. Yeager, Eds., Plenum Publishers, New York, in press.

"One Photon and Two Photon Processes in Chlorophyll a Water Splitting Light Reactions. Reversible and Irreversible Photochemical Pathways," L. M. Fetterman, F. K. Fong and N. Winograd, J. Am. Chem. Soc., submitted.

"Design and Performance of an Energy-and Angle-resolved Secondary Ion Mass Spectrometer," R. A. Gibbs and N. Winograd, Rev. Sci. Instru., 52, 1148 (1981).

"Energy- and Angle-resolved SIMS Investigation of the Ni(001)-Carbon Monoxide System," R. A. Gibbs, S. P. Holland, K. E. Foley, B. J. Garrison and N. Winograd, J. Chem. Phys., 76, 684 (1982).

#### 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The major objective of this work has been to examine the possibility of using secondary ion mass spectrometry (SIMS) coupled with ancilliary modern surface analysis methods as tools to elucidate electrochemical processes. The research effort has been devoted both to understanding the fundamentals of the SIMS process and to applying this information to various surface characterization problems. With this technique a beam of energetic ions, usually  $\text{Ar}^+$  ion, is directed toward the sample. The momentum dissipation that occurs following impact produces secondary ions that can be detected with a mass spectrometer. Of special interest is that the chemical composition of these fragments ought to be related to the chemical composition of the original surface. Since the fragments arise only from the top layers, SIMS is an interesting compliment to other electron spectroscopies such as Auger spectroscopy and ESCA, and to the surface analysis of electrode surfaces.

The major effort was to gain a fundamental understanding of the ion/solid interaction so as to glean maximum information from the spectra. This goal was pursued from two points of view. First, in collaboration with Professor B. J. Garrison of Penn State, they developed a classical dynamics model of the ion impact event which provides semi-quantitative information about the yields of the neutral atoms and molecular clusters that are ejected. The second approach to the problem was to construct an angle and energy-resolved SIMS instrument which selects particles ejected from the surface in certain directions for analysis. With this instrument, the quadrupole mass spectrometer can be rotated with respect to the ion beam, to obtain scans of the yield of ions vs the polar angle. By using single-crystal samples and by making energy and angle-resolved measurements, they made direct comparisons, for the first time, to the predictions of their theory.

As a model system, they chose CO adsorbed onto Ni(001) into a  $c(2 \times 2)$  or  $1/2$  monolayer coverage since  $\text{Ni}^+$  ion yields are very intense from this surface and since model calculations were recently completed. The results showed excellent agreement between the calculated Ni neutral trajectories and the measured  $\text{Ni}^+$  ion yields, if the calculated values are corrected by the presence of a strong image force.

The results have a number of important implications. First, they found that the agreement between theory and experiment is only possible if the CO is bound in a linear or atop bonding configurations. This result was consistent with LEED studies and indicates that angle-resolved SIMS should be an important tool for the characterization of chemisorbed adsorbate geometries. Second, the presence of a strong image force places a number of constraints on proposed theories of the ionization mechanism in SIMS. For example, they found that the ionization probability is reasonably isotropic and independent of particle velocity. These properties virtually rule out the possibility that the ionization occurs by an Auger process as is commonly believed.

AFOSR Program Manager: Denton W. Elliott

RESEARCH EFFORTS COMPLETED IN FY82

SURFACE CHEMISTRY - CAPTAIN LEE E. MYERS

Fundamental Studies of the  
Structure and Chemistry of Solid  
Surfaces  
AFOSR-80-0103

Robert P. Merrill  
School of Chemical Engineering  
Cornell University  
Ithaca, NY 14853

Ion Implantation Studies of  
Titanium Metal  
AFOSR-79-0011

James R. Stevenson  
Keith O. Legg  
Martin W. Ribarsky  
School of Physics  
Georgia Institute of Technology  
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## COMPLETED PROJECT SUMMARY

1. TITLE: Fundamental Studies of the Structure and Chemistry of Solid Surfaces
2. PRINCIPAL INVESTIGATOR: Dr. Robert P. Merrill  
H. F. Johnson Professor of Industrial Chemistry  
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Ithaca, NY 14853
3. INCLUSIVE DATES: 1 July 1977 - 31 December 1980
4. GRANT NUMBER: AFOSR-80-0103
5. COSTS AND FY SOURCE: \$206, 685, FY80
6. SENIOR RESEARCH PERSONNEL: Dr. Herbert Sawin
7. JUNIOR RESEARCH PERSONNEL:

Robert J. Purtell  
Karel K. Czanderna  
Suzan Miller

Masaharu Komiyama  
William Avrin  
Gar B. Hoflund

### 8. PUBLICATIONS:

"A Molecular View of Diffusion and Reaction in Porous Catalysts,"  
R. P. Merrill, Journal of Catalysis, 50, 384 (1977).

"Broad-Frequency Chopper with Adjustable Duty Cycle," H. H. Sawin,  
D. D. Wilkinson, W. M. Chan, S. Smiriga, and R. P. Merrill, J. Vac. Sci.  
Tech., 14, 1205 (1977).

"Reply to Comments of CFSO-BEBO Approach," R. P. Merrill and W. H. Weinberg,  
Journal of Catalysis, 51, 296 (1978).

"Double Rainbow Features in Classical Scattering from Solid Surfaces - Ne on  
Ag(111)," D. R. Dion, J. A. Barker, and R. P. Merrill, Chem. Phys. Lett., 57,  
117 (1980).

"Chemisorption and Reaction of NH<sub>3</sub> on Ni(111)," C. W. Seabury, T. N. Rhodin,  
R. J. Purtell, and R. P. Merrill, Surface Science, 93, 117 (1980).

"Adsorbate Structures from Angle Resolved Photoemission: NH<sub>3</sub> on Ir(111),"  
R. J. Purtell, R. P. Merrill, C. W. Seabury and T. N. Rhodin, Phys. Rev.  
Letters, 44, 1279 (1980).

"Adsorption of Oxygen on Pt(111) and Its Reactivity to Hydrogen and Carbon Monoxide," D. R. Monroe and R. P. Merrill, Journal of Catalysis, 65, 461 (1980).

"Concentration Profiles in Impregnation of Porous Catalysts: Nickel on Alumina," M. Komiyama, R. P. Merrill, and H. F. Harnsberger, Journal of Catalysis, 63, 35 (1980).

"Angularly Resolved Temperature Programmed Decomposition: Nitrogen Emission from the Decomposition of Hydrazine on Ir(111)," H. H. Sawin and R. P. Merrill, J. Chem. Phys., 73, 996 (1980).

"Fourier Analysis of Linear Surface Kinetics in Reactive Molecular Beam Scattering," H. H. Sawin and R. P. Merrill, J. Vac. Sci. and Tech., 19(1) (1981).

"Classical Surface Scattering Computations; Rainbows and Energy Exchange," D. R. Dion, J. A. Barker, and R. P. Merrill, Surface Science, 95, 15 (1980).

"A Semi-Classical Trajectory-Based Calculation of the Multiple Scattering Problem," A. P. Jauho, M. Cohen, J. Wilkins, and R. P. Merrill, to be published in the Proceedings of the Conference on Determination of Surface Structures by LEED, P. M. Marcus and F. Jona, Editors.

"Molecular Orbital Calculations of Atomic Hydrogen Chemisorption on the Beryllium(0001) Surface," G. B. Hoflund and R. P. Merrill, Journal of Physical Chemistry, 85, 2037 (1981).

"Angular Resolved Photoemission from  $\text{NH}_3$  on Ni(110)," K. Jacoby, E. S. Jensen, T. N. Rhodin, and R. P. Merrill, Surface Science, 108, 397 (1981).

"Angular Orientation of  $\text{NH}_3$  on Ni(111) by Low Energy Photoelectron Scattering," W. M. Kung, C. H. Li, S. Y. Tang, C. W. Seabury, K. Jacoby, T. N. Rhodin, R. J. Purtell, and R. P. Merrill, Phys. Rev. Letters, 47, 931 (1981).

"A Kinetic Study of Hydrazine Decomposition on Ir(111) by Molecular Beam Scattering and Temperature Programmed Desorption," H. H. Sawin, Ph.D. Thesis, Cornell University (1980).

"Ammonia Chemisorption on Ir(111)," R. J. Purtell, Ph.D. Thesis, Cornell University (1980).

"Impregnated Nickel on  $\gamma$  Alumina Catalyst: Catalyst Design and Impregnation," M. Komiyama, Ph.D. Thesis, Cornell University (1980).

## 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The primary objective of the work supported by this grant was to examine the decomposition of hydrazine on iridium from a molecular point of view. Since this reaction proceeds very rapidly, reaction probabilities near unity, it is impossible to measure intrinsic kinetics by traditional means at pressures near one atmosphere. Accordingly, this work used reactive molecular beam scattering and temperature programmed desorption techniques. A complimentary approach was to use modern spectroscopic techniques to identify the electronic structure and bonding modes of the surface intermediates in the reaction sequence. Auger spectroscopy, X-ray photoelectron spectroscopy, and ultraviolet photoelectron spectroscopy were used.

The technological objective of this work was to develop enough understanding of the decomposition mechanism to suggest ways of studying the catalyst deactivation and poisoning and to provide guidance on how to develop more stable catalysts. In order to integrate the findings of our fundamental decomposition studies into this technological objective we also examined the problem of reaction and diffusion in porous catalysts from a molecular view and did some work to identify the mechanisms which control the radial concentration profiles which develop when catalysts are made by aqueous impregnation of porous oxide supports.

Using the combination of reactive molecular beam scattering and temperature programmed desorption it has been possible to determine most of the salient features of the reaction sequence of hydrazine decomposition on the (111) face of iridium. The reaction "lights-off" at 200°K to a reaction probability of 0.95 or greater and stays nearly constant up to 1500°K, confirming the remarkable reactivity suggested by the conventional catalytic work. From 200°K up to 500°K the primary decomposition products are  $\text{NH}_3$  and  $\text{N}_2$ . Above 600°K little  $\text{NH}_3$  is produced.

There are at least three parallel channels for the production of  $\text{NH}_3$  in the reaction sequence. All three are simultaneously evident in the experimental transfer function between 500°K and 600°K. Only two are absorbed at temperatures ca. 300°K where the catalyst used in thruster engines is required to "light-off." One has a time constant of several seconds and a branching ratio of 0.95. The other channel has a time constant of ca. 1 m sec., but since it produces only 5% of the  $\text{NH}_3$  product it could never be studied in technological catalysts using standard catalyst testing procedures.

Catalyst deactivation causes disintegration of the catalyst particles in thruster service. This is caused by imbibation of the liquid hydrazine into the pores of the pellet. If the catalyst does not light off within  $10^{-3}$  sec. there is too much liquid uptake and the pressure build-up within the interior of the catalyst exceeds the tensile strength of the pellet before the liquid can be pumped back out of the catalyst. Clearly, then, it is the 5% branch of the decomposition reaction that is responsible for the  $10^{-3}$  sec.

light off, not the main channel which requires several seconds. This is certainly the most significant technological finding of the work. It means that one must study this fast branch to identify the causes of catalyst deactivation and to develop strategies for improving catalyst stability. This will require carefully designed time response studies in the absence of mass transport limitations and will not be possible using steady-state measurements.

Initially, hydrazine adsorbs dissociatively onto the clean iridium surface to produce adsorbed hydrogen atoms and a di-adsorbed di-imide. Adsorption into this state is irreversible and TPD of this species yields  $\text{NH}_3$  and  $\text{N}_2$ . A reversibly adsorbed hydrazine can adsorb onto this di-imide. The decomposition of the di-imide-hydrazine complex to give gas phase  $\text{N}_2$  and two adsorbed  $\text{NH}_3$  comprises one of the decomposition branches, i.e., the slow branch at 300°K. The fast branch at 300°K passes through an  $\text{NH}_2$  adsorbed species which adds adsorbed H to give  $\text{NH}_3$  which subsequently desorbs. The third branch results from successive dehydrogenation of a mono-adsorbed di-nitrogen species and subsequent addition of hydrogen to non-adsorbed nitrogen to give a sort of nitrogen analog of adsorbed methyl isocyanide,  $\text{H}_3\text{N}-\text{N}\equiv\text{IR}$ . This species then decomposes to give gaseous  $\text{NH}_3$  and adsorbed N atoms. This complex reaction sequence has within it fourteen elementary steps. The studies have been able to measure the rate of 13 of these fourteen steps at at least one temperature. Four of the elementary rates have been measured over a sufficiently wide temperature range that both pre-exponentials and activation energies have been determined. The role of surface diffusion is evident in the steps involving adsorbed hydrogen addition and in the slow branch passing through the hydrazine/di-imide complex.

Spectroscopic evidence for  $\text{N}_2\text{H}_4$ ,  $\text{NH}_2$ ,  $\text{NH}_3$  and N surface intermediates has been found. Adsorbed  $\text{NH}_3$  has been characterized most completely.  $\text{NH}_3$  adsorbs through the nitrogen lone pair with the hydrogen triad parallel to the surface. The N-H bonding orbitals are barely shifted by adsorption though the lone pair is stabilized by adsorption. The amount of stabilization of the lone pair on different metals correlates with its chemisorption binding energy. The work function change is very large, -3 eV on a saturated overlayer. This is too large to be attributed only to orientation of the gas phase dipole and implies charge transfer from the lone pair into the iridium metal. The chemisorption binding site is one of the three fold hollows on the (111) surface and the  $\text{NH}_3$  molecule is rotationally oriented by adsorption. There is also a density driven phase transition at ca. 120°K which nucleates a (2x1) surface structure that produces a strong dispersion in the energies of the 1e N-H bonding orbitals as two dimensional energy bands are formed.

Ammonia TPD exhibits three desorption states, but no decomposition to Nitrogen when the surface is scrupulously clean of oxygen. These same three peaks are present, with some changes in relative intensity, when hydrazine is decomposed by temperature programming.

In aqueous impregnation it has been demonstrated that one can control the radial concentration profiles of metal as it is deposited on the interior pore walls of a macroscopic support pellet by adjusting the adsorptivity of the species. A model has been developed which adequately predicts changes in the profiles. One can obtain a uniform profile, a profile where most of the metal is deposited near the exterior of the surface of the catalyst pellet, a sub-surface impregnation, or a band of metal may be deposited with the exterior being free of metal and the center of the pellet also being free of metal. The concepts were demonstrated using nickel solutions impregnated into aluminum spheres. Measurements were made using x-ray fluorescence in an electron microprobe.

AFOSR Program Manager: Lee E. Myers, Capt, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Ion Implantation Studies of Titanium Metal
2. PRINCIPAL INVESTIGATORS: Dr. James R. Stevenson  
Dr. Keith O. Legg  
Dr. Martin W. Ribarsky  
School of Physics  
Georgia Institute of Technology  
Atlanta, GA 30332
3. INCLUSIVE DATES: 1 November 1978 - 31 October 1981
4. GRANT NUMBER: AFOSR-79-0011
5. COSTS AND FY SOURCE: \$57,777, FY79; \$74,229, FY80; \$89,662, FY81
6. JUNIOR RESEARCH PERSONNEL:

J. M. Cathcart  
John M. Merboth  
Mathew J. Rutten  
Donald Hawley

Patricia L. White  
H. Solnick-Legg  
Linda Taylor

### 7. PUBLICATIONS:

"Optical Properties of Titanium and Titanium Oxide Surfaces," William E. Wall, M. W. Ribarsky, and J. R. Stevenson, J. Appl. Phys., 51, 661 (1980).

"Design Considerations for Parasitic Use of Synchrotron Radiation in the Infrared," James R. Stevenson and J. Michael Cathcart, Nuclear Instruments and Methods, 172, 367 (1980).

"A Comparison between the Effects of Implantation in Ultra-Clean and Standard Vacuum Environments," K. O. Legg, M. W. Ribarsky, and J. R. Stevenson, Proceedings of the Conference on Modification of the Surface Properties of Metals by Ion Implantation, Manchester, England (1981).

"Electron Channeling in Ion Implanted Titanium," H. F. Solnick-Legg, K. O. Legg, J. M. Cathcart, and J. R. Stevenson, Proceedings of the Conference on Modification of the Surface Properties of Metals by Ion Implantation, Manchester, England (1981).

### 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The long range objective of this research has been a basic approach to the study of high dose ion implantation in titanium, aluminum and alloys of Ti-Al. The study has included determination of the depth profile of the implanted species and the kinetics of this profile with temperature cycling and grain size changes as well as during oxide and nitride formation. The growth kinetics of oxide and nitride formation was followed in ion implanted specimens to identify important controlling

mechanisms. A new method for measuring radiation damage associated with the implantation process was developed and used to evaluate the effect of damage on growth kinetics and grain size distribution.

Other methods and techniques were used or developed to study the properties of the implanted materials. A far infrared waveguide laser was obtained and used to provide a more precise probe of the oxide formation on titanium surfaces. In addition electron energy loss measurements were made on clean and oxidized titanium surfaces and the technique itself was studied.

The influence of implants on the surface characteristics and oxidation of titanium and the use of various techniques to probe the surface structure were studied. The surface condition of the metal was shown to affect greatly the implant distribution. Erbium implants did not segregate at all to a clean titanium surface but segregated completely to a carbon covered surface. Initial monolayer oxide formation is unaffected by implanted calcium, which does not segregate to the surface. The electronic structure of the oxide layer is, however, unexpectedly complicated, showing features in the electron energy loss spectrum very different from the clean surface. It is shown that care must be taken in studying the loss spectrum itself, especially in identifying the plasmon loss peaks and features associated with the clean surface. It has been found that different implants can seriously affect mechanical strain in the oxide, leading to rumpling and spalling in the case of Ti or Sb implants. These effects appear to be associated with implant segregation to the metal-oxide interface. A semiquantitative electron channeling method has been developed for determining damage levels in implanted materials.

The use and feasibility of synchrotron radiation as an infrared source in new national facilities now under construction has been studied. The use of a far infrared wave-guide laser for probing the structure and kinetics of oxides was also studied.

AFOSR Program Manager: Lee E. Myers, Captain, USAF

RESEARCH EFFORTS COMPLETED IN FY82

MOLECULAR DYNAMICS - MAJOR WILLIAM G. THORPE

Theoretical Studies of Metal  
Oxides  
AFOSR-78-3677

A. Dalgarno  
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Microscopic Theory of Electronic  
Transitions in Molecular Rate  
Processes  
F49620-78-C-0005

Thomas F. George  
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Multiphoton Dynamics: Energy  
Disposal During Decomposition of  
Molecules Under Static and Very Low  
Pressure, Conditions: Specific Rate  
Constants and Distribution Functions  
F49620-78-C-0107

David Golden  
John R. Barker  
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Laboratory Studies of Solvated  
Gas-Phase Anions  
AFOSR-81-0105

Peter M. Hierl  
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Infrared Chemiluminescence Studies  
of Ion-Molecule Reactions in a  
Flowing Afterglow  
AFOSR-78-3565

Stephen R. Leone  
G. Barney Ellison  
Veronica M. Bierbaum  
Dept of Chemistry, Univ of  
Colorado & Joint Inst  
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Study of the Chlorine-Basic Hydrogen  
Peroxide Reaction  
AFOSR-81-0155

Richard J. McCluskey  
Department of Chemical  
Engineering  
Clarkson College of Technology  
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Excited State Chemistry of Halogen  
Azides  
F49620-79-C-0053

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Studies in Non-Equilibrium  
Statistical Mechanics  
AFOSR-78-3724

Computational Study of Nonadiabatic  
Effects in Atom-Molecule  
Reactive Scattering  
F49620-81-C-0046

Studies of Energy Transfer and  
Selective Chemical Reaction  
Using Tunable IR Radiation  
AFOSR-77-3240

Spectroscopy and Chemistry of  
Molecules with High Vibrational  
Energy Content  
AFOSR-78-3725

Radiation and Laser Potential of  
Homo and Heteronuclear Rare-gas  
Diatomic Molecules  
AFOSR-77-3137

Kinetic Studies of Gas Phase  
Free Radicals  
AFOSR-78-3693

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Departments of EE, Physics  
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## COMPLETED PROJECT SUMMARY

1. TITLE: Theoretical Studies of Metal Oxides
2. PRINCIPAL INVESTIGATOR: Professor A. Dalgarno  
Department of Chemistry  
Harvard College Observatory  
Cambridge, MA 02138
3. INCLUSIVE DATES: 30 September 1978 - 31 October 1981
4. CONTRACT NUMBER: AFOSR-78-3677
5. COSTS AND FY SOURCE: \$57,599, FY79; \$60,367, FY80; \$63,138, FY81;
6. SENIOR RESEARCH PERSONNEL:  
  
Dr. Kate Kirby  
Dr. John Rys  
Dr. Shih-I Chu
7. JUNIOR RESEARCH PERSONNEL:  
  
Scott Butler  
Warren Wendt  
Catherine Asaro
8. PUBLICATIONS: None (several are expected on completion of the calculations)
9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Elaborate ab initio calculations of the potential energy curves and molecular eigenfunctions of the low-lying singlet and triplet states of magnesium oxide MgO and of the low-lying doublet states of the positive ion  $\text{MgO}^+$  have been carried out. The electric dipole transition moments connecting the electronic states have been obtained over a wide range of internuclear distances. Limited calculations have been performed of the electric dipole matrix elements between different vibrational levels. The radiative lifetime of the  $B^1\Sigma^+$  state is predicted to be about  $2.1 \times 10^{-8}$  s and of the  $A^1\Pi$  state about  $2.8 \times 10^{-4}$  s. The ionization potential of MgO is predicted to be 7.9 eV.

AFOSR Program Manager: William G. Thorpe, Major, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Microscopic Theory of Electronic Transitions in Molecular Rate Processes
2. PRINCIPAL INVESTIGATOR: Dr. Thomas F. George  
Department of Chemistry  
The University of Rochester  
Rochester, NY 14627
3. INCLUSIVE DATES: 15 November 1977 - 14 November 1981
4. GRANT NUMBER: F49620-78-C-0005
5. COSTS AND FY SOURCE: \$72,000, FY78; \$75,000, FY79; \$80,693, FY80;  
\$83,000, FY81

6. SENIOR RESEARCH PERSONNEL:

Dr. John C. Bellum	Dr. Jit-teng Lin
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Dr. Dilip K. Bhattacharyya	Dr. Sanboh Lee
Dr. Cheng-hui Chang	Dr. William C. Murphy
Dr. Paul L. DeVries	Dr. Mark S. Slutsky
Dr. Michael Hutchinson	Dr. Jian-Min Yuan
Dr. Kai-Shue Lam	

7. JUNIOR RESEARCH PERSONNEL:

Mr. Ranco Battaglia  
Dr. Jui-teng Lin

8. PUBLICATIONS:

"Quantum-Mechanical Theory Including Angular Momentum Analysis of Atom-Atom Collisions in a Laser Field," P. L. DeVries and T. F. George, Mol. Phys., 36, 151 (1978).

"Quantum Theory of Laser-Stimulated Desorption," M. S. Slutsky and T. F. George, Chem. Phys. Lett., 57, 474 (1978).

"Penning Ionization of Ar by He\*(1s2s,<sup>3</sup>S) in the Presence of Intense Laser Radiation: Pronounced Laser-Modified Collisional Effects in the Emitted-Electron Energy Spectrum," J. C. Bellum, K. S. Lam and T. F. George, J. Chem. Phys., 69, 1781 (1978).

"A Semiclassical Approach to Collisional Ionization with Application to the Ar-He System," K. S. Lam, J. C. Bellum and T. F. George, Chem Phys., 33, 219 (1978).

"Molecular Collisions in a Laser Field: Effect of the Laser Linewidth," H. W. Lee, P. L. DeVries and T. F. George, J. Chem. Phys., 69, 2596 (1978).

"Is Photon Angular Momentum Important in Molecular Collision Processes Occurring in a Laser Field?" P. L. DeVries and T. F. George, Phys. Rev. A, 18, 1751 (1978).

"A Quantum-Mechanical Method for Calculating Level Widths and Shifts, Applicable to Type I Unimolecular Predissociation," I. H. Zimmerman, J. M. Yuan and T. F. George, Mol. Phys., 36, 1675 (1978).

"Molecular Collisions in a Multimode Laser Field: Computational Study of the Effect of Time Variation in the Laser Intensity," H. W. Lee, P. L. DeVries, I. H. Zimmerman and T. F. George, Mol. Phys., 36, 1693 (1978).

"Semiclassical Study of Reactive Scattering in a Laser Field:  $F + H_2 + \hbar\omega$  ( $1.06\mu m$ ) System," J. M. Yuan and T. F. George, J. Chem. Phys., 70, 990 (1979).

"Laser-Stimulated Migration of Adsorbed Atoms on Solid Surfaces," M. S. Slutsky and T. F. George, J. Chem. Phys., 70, 1231 (1979).

"Overview of Laser Applications to Chemistry," T. F. George, Opt. Eng., 18, 167 (1979).

"Theory of Molecular Rate Processes in the Presence of Intense Laser Radiation," T. F. George, I. H. Zimmerman, P. L. DeVries, J. M. Yuan, K. S. Lam, J. C. Bellum, H. W. Lee, M. S. Slutsky and J. Lin, in Chemical and Biochemical Application of Lasers, Vol. IV, C. B. Moore, Ed. (Academic Press, New York, 1979), pp 253-354.

"Molecular Collision Processes in the Presence of Picosecond Laser Pulses," H. W. Lee and T. F. George, J. Phys. Chem., 83, 928 (1979).

"High-Energy Approximation for Atom-Surface Elastic Scattering," H. W. Lee and T. F. George, J. Chem. Phys., 70, 3685 (1979).

"Energy Transfer in Gas-Surface Scattering in the Presence of a Laser Field," H. W. Lee and T. F. George, J. Chem. Phys., 70, 4220 (1979).

"On the Interweaving of Partial Cross Sections of Different Parity," P. L. DeVries and T. F. George, Chem. Phys. Lett., 63, 240 (1979).

"Collisional Ionization in the Presence of Intense Laser Radiation: Quantum-Mechanical Calculations for  $He^*(^3S) + Ar \pm \hbar\omega \rightarrow Ar^+(^2P) + e^-$ ," J. C. Bellum and T. F. George, J. Chem. Phys., 70, 5059 (1979).

"An Angular Momentum Approximation for Molecular Collisions in the Presence of Intense Laser Radiation," P. L. DeVries and T. F. George, Mol. Phys., 38, 561 (1979).

"Quantum Mechanical Calculation of Three-Dimensional Atom-Diatom Collisions in the Presence of Intense Laser Radiation," P. L. DeVries and T. F. George, J. Chem. Phys., 71, 1543 (1979).

"Kinetic Model of Laser-Controlled Heterogeneous Processes," J. Lin and T. F. George, Chem. Phys. Lett., 66, 5 (1979).

"A New Propagation Method for the Radial Schrodinger Equation," P. L. DeVries, Chem. Phys. Lett., 66, 258 (1979).

"Atom-Surface Elastic Scattering in the Presence of Laser Radiation," H. W. Lee and T. F. George, Theoret. Chim. Acta (Berl.), 53, 193 (1979).

"F + H<sub>2</sub> Collisions on Two Electronic Potential Energy Surfaces: Quantum-Mechanical Study of the Collinear Reaction," I. H. Zimmerman, M. Baer, and T. F. George, J. Chem. Phys., 71, 4132 (1979).

"Molecular Collisions in a Laser Field: Basis Set Selection and the Rotating-Wave Approximation," P. L. DeVries, K. S. Lam and T. F. George, Int. J. Quantum Chem., Symp. No. 13, 541 (1979).

"F + H<sub>2</sub> Collisions in the Presence of Intense Laser Radiation: Reactive and Nonreactive Processes," P. L. DeVries, T. F. George and J. M. Yuan, Faraday Disc. Chem. Soc., 67, 90 (1979).

"Theory of the Interaction of Laser Radiation with Molecular Dynamical Processes Occurring at a Solid Surface," T. F. George, J. Lin, K. S. Lam and C. Chang, Opt. Eng., 19, 100 (1980).

"Atomic and Molecular Collisions in the Presence of Strong Radiation Fields," P. L. DeVries, K. S. Lam and T. F. George, in Electronic and Atomic Collisions, N. Oda and K. Takayanagi, Eds. (North-Holland, Amsterdam, 1980), pp. 683-695.

"Na + Xe Collisions in the Presence of Two Nonresonant Lasers," P. L. DeVries, C. Chang, T. F. George, B.C.F. Laskowski and J. R. Stallcop, Chem. Phys. Lett., 69, 417 (1980).

"Quantum-Stochastic Approach to Laser-Stimulated Desorption Dynamics and Population Distributions of Chemisorbed Species on Solid Surfaces," J. Lin and T. F. George, J. Chem. Phys., 72, 2554 (1980).

"A New Propagation Method for the Radial Schrodinger Equation: Application to Close-Coupled Equations," P. L. DeVries and T. F. George, Mol. Phys., 39, 701 (1980).

"Semiclassical Theory of Electronically Nonadiabatic Transitions in Molecular Collision Processes," K. S. Lam and T. F. George, in Semiclassical Methods in Molecular Scattering and Spectroscopy, M. S. Child, Ed. (D. Reidel, Dordrecht-Holland, 1980), pp. 179-261.

"Semiclassical Study of the Quenching of Excited-State Fluorine Atom by Hydrogen Molecule: Comparison between Reactive and Nonreactive Processes," J. M. Yuan, T. F. George, G. M. Skuse, R. L. Jaffe, A. Komornicki and K. Morokuma, Isr. J. Chem., 19, 337 (1980).

"A New Semiclassical Decoupling Scheme for Resonance Effects in Vibrational-to-Electronic Energy Transfer Collision Processes," H. W. Lee, K. S. Lam, P. L. DeVries and T. F. George, J. Chem. Phys., 73, 206 (1980).

"Computational Study of Alkali-Metal-Noble-Gas Collisions in the Presence of Nonresonant Lasers:  $\text{Na} + \text{Xe} + \hbar\omega_1 + \hbar\omega_2$  System," P. L. DeVries, C. Chang, T. F. George, B. Laskowski and J. R. Stallcop, Phys. Rev. A, 22, 545 (1980).

"Effects of Surface Magnetic Fields on Laser-Induced Predissociation of Diatomic Molecules," D. K. Bhattacharyya, K. S. Lam and T. F. George, J. Chem. Phys., 73, 1999 (1980).

"Multiphoton-Multiphonon Theory of Laser-Stimulated Surface Processes," J. Lin, A. C. Beri, M. Hutchinson, W. C. Murphy and T. F. George, Phys. Lett., 79A, 233 (1980).

"Dynamical Model of Selective versus Nonselective Laser-Stimulated Surface Processes," J. Lin and T. F. George, Surface Sci., 100, 381 (1980).

"Dynamical Model of Selective vs. Nonselective Laser-Stimulated Surface Processes. 2. Analytical Methods and Applications to Surface Rate Processes," J. Lin and T. F. George, J. Phys. Chem., 84, 2957 (1980).

"Generalized Langevin Theory of Multiphoton Absorption Dynamics of Polyatomic Molecules and the Nature of Laser-Selective Effects," J. Lin and T. F. George, Phys. Lett., 80A, 296 (1980).

"Laser Interaction with the End Atoms of a Linear Chain," W. C. Murphy and T. F. George, Surface Sci., 102, L46 (1981).

"High-Energy Positron Ionization of Adsorbed Species in the Impulse Approximation," K. S. Lam and T. F. George, J. Phys. Chem., 85, 317 (1981).

"Spectroscopy of Quasibound States formed by Molecular Collisions in the Presence of a Laser," M. Hutchinson and T. F. George, Phys. Lett., 82A, 119 (1981).

"Quantum Dynamical Model of Laser/Surface-Induced Predissociation: Multiphoton-Multiphonon Processes and Photon/Phonon-Dressed States," J. Lin and T. F. George, Surface Sci., 107, 417 (1981).

"Surface Magnetic Field/Laser Synergistic Effects on the Predissociation of Adsorbed Diatomic Molecules," D. K. Bhattacharyya, K. S. Lam and T. F. George, J. Chem. Phys., 75, 203 (1981).

"Classical Model of Laser-Stimulated Surface Processes: Energy Absorption Profiles via the Langevin Equation," J. Lin and T. F. George, Phys. Rev. B, 24, 64 (1981).

"Semiclassical Approach to Spontaneous Emission of Molecular Collision Systems: A Dynamical Theory of Fluorescence Line Shapes," K. S. Lam and T. F. George, J. Chem. Phys., in press.

"Computational Study of Alkali-Metal Noble-Gas Collisions in the Presence Nonresonant Lasers. II. Na + Ar +  $\hbar\omega_1 + \hbar\omega_2$  System," P. L. DeVries and T. F. George, Mol. Phys., in press.

"Microscopic Theory of Electronic Transitions in Molecular Rate Processes," T. F. George, Final Technical Report.

## 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives were to help establish a theoretical foundation for the description of gas-phase molecular rate processes involving electronic transitions, both in the absence (field-free) and in the presence of an external laser field. Such processes can be viewed in terms of the dynamic interaction between two or more potential energy surfaces. For field-free processes (Part I below) this interaction is associated with the coupling between electronic and nuclear degrees of freedom, and for processes in a laser field (Part II) this coupling occurs in conjunction with radiative coupling. During the course of the research, an interest developed in laser-stimulated molecular rate processes occurring at a gas-surface interface (not necessarily involving electronic transitions), and this is mentioned in Part III.

### I. Field-Free Processes

A fully quantum mechanical (coupled-channel) calculation was carried out for the reaction  $F + H_2 \rightarrow HF + H$  restricted to collinear collisions. The calculation included the coupling of two potential energy surfaces, where the ground-state surface correlates from  $F(^2P_{3/2}) + H_2$  to  $HF(^1\Sigma^+) + H$  and the excited-state surface from  $F(^2P_{1/2}) + H_2$  to a set of excited electronic states of HF which are not energetically accessible for collision energies of chemical interest. A conclusion drawn from the results is that the dynamics associated with transitions between surfaces, occurring in the reactant region, is essentially decoupled from the dynamics associated with chemical rearrangement in the reaction barrier region. Removing the restriction to collinear collisions but then restricting the study to nonreactive collisions, a fully quantum mechanical calculation was carried out for the quenching process  $F(^2P_{1/2}) + H_2 \rightarrow F(^2P_{3/2}) + H_2$  for three-dimensional collisions, with  $H_2$  considered as a rigid rotor. There is a near-resonant electronic-to-rotational energy transfer process when  $H_2$  makes a transition from its ground to its second-excited rotational state, and plots of partial cross sections of different parity (even and odd) vs. total angular momentum are seen to interweave with each other. In addition to the above quantum mechanical studies, semiclassical methods, where the nuclear degrees of freedom are treated classically, were refined for describing resonant vibrational-to-electronic energy transfer in model atom-diatom collision systems.

### II. Laser-Stimulated Gas-Phase Processes

With sufficient power density (typically greater than a  $MW/cm^2$ , although as low as a  $kW/cm^2$  for special cases - see Part II.B.4), a laser can

actually interact directly with the dynamics of a molecular collision process. The focus has been on situations where a laser photon comes into resonance between two potential energy surfaces during the course of a collision. It is important to realize that the resonance need not occur between asymptotic levels of individual reactants or products.

#### A. Theory

The theory has been refined to include specific characteristics of the laser field. One characteristic is the photon angular momentum, which couples different total molecular angular momentum states. Since the space-fixed projections of the molecular angular momentum are no longer conserved, an exact solution of the problem is intractable due to the huge number of coupled-channel equations. An approximation has been developed, which averages over the angular dependence of various matrix elements, in order to substantially reduce the number of coupled equations without a significant loss in accuracy. Other laser characteristics considered were the line width, pulse shape, multiple modes and the effect of time variation in the intensity. Provided the average laser intensity is less than  $10 \text{ GW/cm}^2$ , the single-mode approximation is seen to be very accurate.

#### B. Applications

1. Energy Transfer Quantum coupled-channel calculations were carried out for  $\text{Na} + \text{Xe}$  collisions in the presence of two lasers: the rhodamine-110 dye laser ( $0.55 \mu\text{m}$ ) and the Nd:glass laser ( $1.32 \mu\text{m}$ ). The two lasers are not resonant with the asymptotic atomic states but do come into resonance with the molecular electronic states for finite internuclear separations. For intensities of each laser at  $10 \text{ MW/cm}^2$ , the cross sections for the single-photon excitation of  $\text{Na}(3s)$  to  $\text{Na}^*(3p)$  and the two-photon excitation to  $\text{Na}^*(4s)$  are as high as  $0.3$  and  $0.0008 \text{ \AA}^2$ , respectively. Calculations were carried out for  $\text{Na} + \text{Ar}$  in the presence of the two lasers, with results similar to those for  $\text{Na} + \text{Xe}$ . Calculations were also carried out for three-dimensional nonreactive  $\text{F}^*(^2P_{1/2}) + \text{H}_2$  (rigid rotor) collisions, where the presence of a laser field is seen to enhance the quenching cross section.

2. Chemical Reaction A semiclassical calculation was performed for the collinear  $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$  reaction in the presence of a Nd:glass laser ( $1.06 \mu\text{m}$ ). While the laser comes into resonance between two potential energy surfaces, the reactive process involves no net photon absorption (i.e., the photon acts as a "catalyst"). No appreciable effect of the laser is observed until the intensity is raised higher than a  $\text{TW/cm}^2$ , where the branching ratio  $\text{HF}(v=3)/\text{HF}(v=2)$  changes from less than unity to greater than unity. The reason for the high laser intensity threshold is twofold: (1) the photon catalytic process is second-order, and (2) the shapes of the two potential energy surfaces are significantly different from each other in the region of resonance with the laser.

3. Collisional Ionization Fully quantum mechanical calculations have been carried out for the laser-modified Penning ionization process where



Ar undergoes ionization by collision with  $\text{He}^*(3S)$ . The excited-state potential curve correlating to  $\text{He}^* + \text{Ar}$  is embedded in the electronic continuum, and the laser couples discrete and continuum electronic states. There is a field-free peak in the emitted-electron energy spectrum which exists in the presence of the laser, and the laser produces two additional peaks on either side of the field-free peak, which are separated by  $2\hbar\omega$ . The lower-energy peak corresponds to stimulated photon emission while the higher-energy peak corresponds to photon absorption. Two separate calculations were carried out using the  $10.6\text{-}\mu\text{m}$  line of a  $\text{CO}_2$  laser and the  $1.315\text{-}\mu\text{m}$  line of the iodine atom laser. Experimentally measurable results are predicted for laser intensities less than  $200 \text{ MW/cm}^2$ .

4. Transition State Spectroscopy A quantum mechanical theory has been developed to describe the spectroscopy of quasibound molecules in a laser field. One laser is used to link two electronic states of the collision system, giving rise to a set of field-dressed quasibound states which can be spectroscopically probed by a second laser. Calculations were carried out for  $\text{Xe} + \text{F}$  collisions, where the first laser was in the ultraviolet region ( $305\text{-nm}$  line of the  $\text{XeCl}$  laser) and the second was in the infrared region. Provided that the collision energy is properly chosen, reasonably high total cross sections (up to  $1 \text{ \AA}^2$ ) can be achieved at fairly low intensities for both lasers (down to  $1 \text{ kW/cm}^2$ ).

### III. Laser-Stimulated Gas-Surface Processes

As a first step toward understanding how laser radiation might affect or induce rate processes at a gas-surface interface, quantum mechanical models have been developed to study infrared photon energy absorption by an adspecies with subsequent desorption and/or migration. Desorption is possible with laser intensities as low as  $10 \text{ W/cm}^2$ , and both multiphoton and multiphonon effects have been considered. A kinetic model suggests that the measurement of the partial pressure of selectively excited adspecies as a function of laser intensity can yield information on properties such as coverage of the adsorbate and the structure of the adsorbent surfaces. A classical model based on a linear chain has also been developed for the laser excitation of the  $\text{O-Si}$  and  $\text{H-Pb}$  adspecies-surface systems; the laser intensity required to achieve desorption is weakly sensitive to the surface chain length (for four or more atoms).

The cooperative role of a surface and high-power visible and ultraviolet laser radiation in the predissociation of diatomic molecules has been studied semiclassically for  $\text{H}_2$ ,  $\text{NO}$  and  $\text{O}_2$  adsorbed on metal surfaces. The theoretical approach includes the effect of the surface magnetic field, which leads to Zeeman splitting of the multiplet molecular terms. There is an enhancement of the predissociation rate due to the adsorbent, as compared with pure gas-phase laser-induced predissociation. While the enhancement persists for  $\text{H}_2$  and  $\text{NO}$  as the laser intensity increases, there is a diminution for  $\text{O}_2$  as compared with the gas-phase situation.

A classical perturbation treatment of atom-surface scattering in the presence of a laser field has been performed, where the laser frequency is chosen to directly excite a surface vibration. The energy transfer to the surface can be expressed as the sum of the energy transfer by the gas atom, the energy transfer by the laser and an interference term. Under certain limiting conditions, such as a high velocity of the gas atom or a short-range gas-surface interaction, the interference is constructive (i.e., positive) if the laser frequency is greater than the surface vibrational frequency and destructive (i.e., negative) if the laser frequency is less than the surface vibrational frequency.

AFOSR Program Manager: William G. Thorpe, Major, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Multiphoton Dynamics: Energy Disposal During Decomposition of Molecules Under Static and Very Low Pressure, Conditions: Specific Rate Constants and Distribution Functions.
2. PRINCIPAL INVESTIGATORS: Dr. David Golden  
Dr. John R. Barker  
SRI International  
Menlo Park, CA 94025
3. INCLUSIVE DATES: 12 May 1978 - 14 May 1982
4. CONTRACT NUMBER: F49620-78-C-0107
5. COSTS AND FY SOURCE: \$30,000, FY78; \$119,182, FY79; \$131,908, FY80;  
\$84,452, FY81; \$48,172, FY82
6. SENIOR RESEARCH PERSONNEL: Dr. Alan C. Baldwin  
Dr. Michel Rossi
7. PUBLICATIONS:

"Infrared Multiphoton Chemistry: Comparison of Theory and Experiment. Solution of the Master Equation," A. C. Baldwin, J. R. Barker, D. M. Golden, R. Duperrex, and H. van den Bergh, Chem. Phys. Lett., 62, 178 (1979).

"Infrared Multiphoton Dissociation Yields via a Versatile New Technique. Intensity, Fluence, and Wavelength Dependence for  $CF_3I$ ," M. J. Rossi, J. R. Barker, and D. M. Golden, Chem. Phys. Lett., 65, 523, 1979.

"Infrared Multiphoton Generation of Radicals: A New Technique for Obtaining Absolute Rate Constants. Application to Reactions of  $CF_3$ ," M. J. Rossi, J. R. Barker, and D. M. Golden, J. Chem. Phys., 71, 3722, 1979.

"Infrared Multiphoton Decomposition: A Comparison of Approximate Models and Exact Solutions of the Energy-Grained Master Equation," J. R. Barker, J. Chem. Phys., 72, 3686, 1980.

"Application of a New Technique to Infrared Laser Multiphoton Dissociation of Molecules," J. R. Barker, M. J. Rossi, A. C. Baldwin and D. M. Golden, Proceedings of the International Conference on Lasers '79, December 17-21, 1979, pp 251-257.

"Infrared Multiphoton Decomposition: Photochemistry and Photophysics," D. M. Golden, M. J. Rossi, A. C. Baldwin, and J. R. Barker, Accounts of Chemical Research, 14, 56 (1981).

"IR Photochemistry: A Unified Approach for Single-Channel Reactions. I. Theory and Computational Examples," A. C. Baldwin and J. R. Barker, J. Chem. Phys., 74, 3813 (1981).

"IR Photochemistry: A Unified Approach for Single-Channel Reactions. II. Treatment of Experimental Data," A. C. Baldwin and J. R. Barker, J. Chem. Phys., 74, 3823 (1981).

"Infrared Multiphoton Photophysics: Decomposition of  $C_nF_{2n+1}I$  ( $n = 1, 2, 3$ )," M. J. Rossi, J. R. Barker and D. M. Golden, J. Chem. Phys., 76, 406 (1982).

"IR Photochemistry: A Unified Approach for Single-Channel Reactions. III. A Simple Approximate Solution of the Master Equation," A. C. Baldwin and J. R. Barker, Chem. Phys. Lett., 86, 55 (1982).

"Laser-Induced Chemical Kinetics: Absolute Rate Constants for the Reactions  $C_2F_5 + Br_2 \rightarrow C_2F_5Br + Br$  and  $n-C_3F_7 + Br_2 \rightarrow n-C_3F_7Br + Br$ ," M. J. Rossi, J. R. Barker, and D. M. Golden, Int. J. Chem. Kinetics, 14, 499 (1982).

Review papers, which are in part concerned with work undertaken here, are:

"Experimental and Theoretical Examples of the Value and Limitations of Transition State Theory," D. M. Golden, J. Phys. Chem., 83, 108 (1979).

"Measurement and Estimation of Rate Constants," D. M. Golden, Dynamics and Modeling of Reactive Systems, Warren E. Stewart, W. Harmon Ray, and Charles C. Conley, Eds., pp. 315-331 (Academic Press, New York, 1980).

"Thermochemistry and Kinetics of Aromatic Radicals," D. M. Golden, Frontiers of Free Radical Chemistry, William A. Pryor, Ed., pp. 31-41 (Academic Press, New York, 1980).

"Measurement and Estimation of Rate Constants for Modeling Reactive Systems," in Modeling of Chemical Reaction Systems, Proceedings of an International Workshop, Heidelberg, Fed. Rep. of Germany, 1-5 September 1980, K. H. Ebert, P. Deuflhard, and W. Jager, Eds., pp. 148-161 (Springer-Verlag, Berlin, 1981).

#### 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

An energy-grained master equation has been used to model the multiphoton pumping process in  $SF_6$ . It was found that an energy-dependent absorption cross section that was approximately inversely dependent on the level of excitation was needed to reproduce experimental data on the fraction decomposed per pulse. Intensity, fluence, and wavelength dependence of the collisionless infrared multiphoton dissociation yield for  $CF_3I$  have been determined via 'titration' of radical photon products and molecular-beam-sampling-mass spectrometry. The importance of nonlinear effects in the pumping of this molecule was confirmed. The intensity, fluence, and wavelength dependence of the collisionless

infrared multiphoton yield of a series of perfluorinated alkyl iodides ( $\text{CF}_3\text{I}$ ,  $\text{C}_2\text{F}_5\text{I}$ ,  $\text{C}_3\text{F}_7\text{I}$ ) have been studied. Continuing work on energy-grained master equation approaches to understanding multiphoton phenomena has provided a powerful method for analyzing and comparing data based on a cumulative log-normal probability distribution for the multiphoton yield. The infrared multiphoton dissociation of  $\text{CF}_3\text{I}$  was used as a convenient source of  $\text{CF}_3$  radicals under very low-pressure conditions. Measurements of thermal absolute rate constants at 298 K for the reactions  $\text{CF}_3$  plus  $\text{Br}_2$  yielding  $\text{CF}_3\text{Br}$  and  $\text{Br}$ ,  $\text{CF}_3$  plus  $\text{ClNO}$  yielding  $\text{CF}_3\text{Cl}$  plus  $\text{NO}$ ,  $\text{CF}_3$  plus  $\text{O}_3$  yielding  $\text{CF}_3\text{O}$  plus  $\text{O}_2$ , and  $\text{CF}_3$  plus  $\text{NO}_2$  yielding  $\text{CF}_3\text{O}$  plus  $\text{NO}$  yield  $7.8 \times 10^8$ ,  $3.5 \times 10^8$ ,  $5.6 \times 10^0$ , and  $1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. This new technique shows great promise for production of other free radicals of interest and measurement of thermal absolute rate constants over a wide temperature range. The most recent work has centered on studying the thermochemistry of the tertiary butyl radical whose heat of formation and entropy were determined to be  $6.9 \pm 0.5 \text{ kcal/mol}$  and  $70.2 \pm 1.0 \text{ Gibbs/mol}$  respectively.

AFOSR Program Manager: William G. Thorpe, Major, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Laboratory Studies of Solvated Gas-Phase Anions

2. PRINCIPAL INVESTIGATOR: Prof. Peter M. Hierl  
Department of Chemistry  
University of Kansas  
Lawrence, KS 66045

3. INCLUSIVE DATES: 1 March 1981 - 28 February 1982

4. GRANT NUMBER: AFOSR-81-0105

5. COSTS AND FY SOURCE: \$9,944, FY82 (Mini Grant)

6. PUBLICATIONS:

"Translational Energy Dependence of Cross Sections for Reactions of  $\text{OH}^-(\text{H}_2\text{O})_n$  with  $\text{CO}_2$  and  $\text{SO}_2$ ," John F. Paulson and Peter M. Hierl, to be submitted to J. Chem. Phys.

"Effect of Reactant Ion Solvation on Gas-Phase  $\text{S}_\text{N}2$  Reactions," John F. Paulson, Michael J. Henchman, and Peter M. Hierl, to be submitted to J. Chem. Phys.

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this project was to investigate the kinetics of the reactions of solvated ions such as  $\text{OH}^-(\text{H}_2\text{O})_n$ , where  $n$  extends from 0 to 3, with neutral molecules of atmospheric importance such as  $\text{CO}_2$  and  $\text{SO}_2$ . A tandem mass spectrometer was used to measure reaction cross sections as a function of reactant translational energy over the range 0.15-25.0 eV (LAB). The reactions observed include solvent switching, collision-induced dissociation, and charge transfer. The exothermic solvent switching reactions are very rapid, having cross sections which approach several hundred square Angstroms at low energies. These cross sections decrease with translational energy  $E_\text{T}$  approximately as  $E_\text{T}^{-0.5}$  up to 1 eV and then decrease much more rapidly at higher collision energies. Estimates of bond dissociation energies for the cluster ions are derived from the measured translational energy thresholds for the endothermic collisional dissociation processes.

AFOSR Program Manager: William G. Thorpe, Major, USAF

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CHEMICAL & ATMOSPHERIC SCI.(U) AIR FORCE OFFICE OF  
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CHEMICAL & ATMOSPHERIC SC. (U) AIR FORCE OFFICE OF  
SCIENTIFIC RESEARCH BOLLING AFB DC W G THORPE ET AL.  
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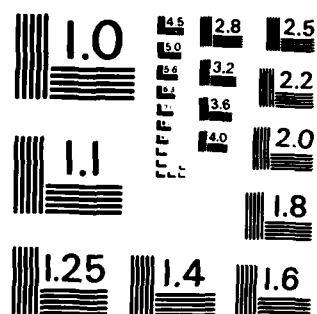
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## COMPLETED PROJECT SUMMARY

1. TITLE: Infrared Chemiluminescence Studies of Ion-Molecule Reactions in a Flowing Afterglow
2. PRINCIPAL INVESTIGATORS: Dr. Stephen R. Leone  
Dr. G. Barney Ellison  
Dr. Veronica M. Bierbaum  
Dept. of Chemistry, University of Colorado  
and Joint Inst. for Laboratory Astrophysics  
University of Colorado and National Bureau of Standards  
Boulder, CO 80309
3. INCLUSIVE DATES: 1 April 1978 - 30 September 1982
4. CONTRACT NUMBER: AFOSR-78-3565
5. COSTS AND FY SOURCE: \$87,987, FY78; \$53,981, FY79; \$51,150, FY80;  
\$170,650, FY81; \$100,000, FY82
6. SENIOR RESEARCH PERSONNEL:  
  
Dr. J. H. Futrell (Visiting Scientist, University of Utah)  
Dr. C.J.S.M. Simpson (Visiting Scientist, Oxford University)  
Dr. Z. Herman (Visiting Scientist, Czechoslovakian Academy of Science)
7. JUNIOR RESEARCH PERSONNEL:  
  
T. S. Zwier                      M. A. Smith  
J. C. Weisshaar                C. E. Hamilton  
M. M. Maricq                   M. A. Duncan
8. PUBLICATIONS:  
  
"Vibrational Chemiluminescence from Ion-Molecule Reactions:  $O^- + CO \rightarrow CO_2^+ + e^-$ ," V. M. Bierbaum, G. B. Ellison, J. H. Futrell and S. R. Leone, J. Chem. Phys., **67**, 2375 (1977).  
  
"Direct Detection of the Product Vibrational-State Distribution in the Associative Detachment Reaction  $Cl^- + H \rightarrow HCl(v) + e^-$ ," T. S. Zwier, M. M. Maricq, C.J.S.M. Simpson, V. M. Bierbaum, G. B. Ellison, and S. R. Leone, Phys. Rev. Lett., **44**, 1050 (1980).  
  
"Vibrational Product State Distributions of Ion-Molecule Reactions by Infrared Chemiluminescence:  $Cl^- + HBr, HI \rightarrow HCl(v) + Br^-, I^-$ ," T. S. Zwier, V. M. Bierbaum, G. B. Ellison, and S. R. Leone, J. Chem. Phys., **72**, 5426 (1980).  
  
"Vibrational Product States from Reactions of  $CN^-$  with the Hydrogen Halides and Hydrogen Atoms," M. M. Maricq, M. A. Smith, C.J.S.M. Simpson, and G. B. Ellison, J. Chem. Phys., **74**, 6154 (1981).

"Nascent Product Vibrational State Distributions of Ion-Molecule Reactions: The Proton Transfer Reactions  $F^- + HX \rightarrow HF(v) + X^-$ ,  $X = Cl, Br, \text{ and } I$ ," J. C. Weisshaar, T. S. Zwier, and S. R. Leone, J. Chem. Phys., **75**, 4873 (1981).

"Nascent Product Vibrational State Distributions of Ion-Molecule Reactions: The  $H + F^- \rightarrow HF(v) + e^-$  Associative Detachment Reaction," T. S. Zwier, J. C. Weisshaar, and S. R. Leone, J. Chem. Phys., **75**, 4885 (1981).

"Infrared Fluorescence: A Versatile Probe of State-Selected Chemical Dynamics," S. R. Leone, Acc. Chem. Res., in press.

"Product Vibrational State Distributions in Thermal Energy Associative Detachment Reactions:  $F^- + H, D \rightarrow HF(v), DF(v) + e^-$ ," M. A. Smith and S. R. Leone, J. Chem. Phys., in press.

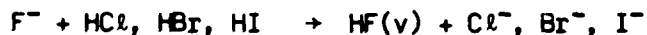
"Flowing Afterglow Studies of Ion Reaction Dynamics Using Infrared Chemiluminescence and Laser-Induced Fluorescence," V. M. Bierbaum, G. B. Ellison, and S. R. Leone, Gas Phase Ion Chemistry, Vol 3, "Ions and Light," M. T. Bowers, Ed., in press.

"Infrared Chemiluminescence from Vibrationally Excited  $NO^+$ : Product Branching in the  $N^+ + O_2$  Ion-Molecule Reaction," M. A. Smith, V. M. Bierbaum, and S. R. Leone, Chem. Phys. Lett., in press.

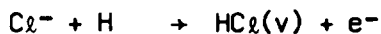
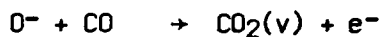
"Ion Collision Dynamics in a Drift Tube Studied with Laser-Induced Fluorescence: The Energy Dependent Rotational State Distribution of  $N_2^+$ ," M. A. Duncan, V. M. Bierbaum, G. B. Ellison and S. R. Leone, J. Chem. Phys., in preparation.

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A versatile new method has been developed for studying the dynamics of thermal energy ion-molecule reactions. Ion reactions are carried out in a well-characterized, state-of-the-art flowing afterglow apparatus and the excited products are monitored optically. Two complementary techniques are used: direct observation of wavelength dispersed infrared chemiluminescence and laser-induced fluorescence detection, i.e., laser excitation of the product molecules to bound electronic states and detection of the resulting visible fluorescence. The initial vibrational distributions have been determined for products formed in a variety of ion-molecule processes, including proton transfer



associative detachment



and heavy atom transfer



In the proton transfer and associative detachment reactions there is efficient channeling of the reaction exothermicity into product vibration. In all cases the highest vibrational state allowed by the available energy is populated and the average fraction of energy deposited in vibration is significantly greater than would be expected by a statistical "prior" distribution.

The heavy atom transfer reaction of  $\text{N}^+ + \text{O}_2$  is sufficiently exothermic to allow formation of electronically excited atomic products,  $\text{O}(^1\text{D})$  and  $\text{O}(^1\text{S})$ . The distribution of the observed infrared chemiluminescence suggests that although there is substantial vibrational excitation of  $\text{NO}^+$ , the channels producing electronic excitation of oxygen atom are preferred.

Collisional excitation and relaxation of ions in a drift tube has been probed by laser-induced fluorescence. For  $\text{N}_2^+$  in helium buffer gas, rotational excitation/relaxation processes are very rapid and equilibrium is achieved in less than ten collisions. The internal energy of the ion is exactly characterized by the center-of-mass energy of the ion-neutral collision.

AFOSR Program Manager: William G. Thorpe, Major, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Study of the Chlorine-Basic Hydrogen Peroxide Reaction
2. PRINCIPAL INVESTIGATOR: Dr. Richard J. McCluskey  
Department of Chemical Engineering  
Clarkson College of Technology  
Potsdam, NY 13676
3. INCLUSIVE DATES: 30 June 1981 - 29 September 1982
4. GRANT NUMBER: AFOSR-81-0155
5. COSTS AND FY SOURCE: \$10,000, FY81 (Mini Grant)
6. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The reaction of chlorine with alkaline hydrogen peroxide solutions, approximately 2.5M in  $O_2H^-$ , has been examined in an unagitated batch reactor at 10°C. Initial chlorine partial pressures of up to 450 torr and reaction times of one, three and six minutes were investigated. The results are qualitatively in agreement with the theory for absorption with an instantaneous reaction, in which the rate of reaction becomes controlled by liquid phase mass transfer after an initial, rapid reaction depletes the interfacial region of  $O_2H^-$  reactant.

The effective anion diffusivity was on the order of  $7 \times 10^{-4} \text{ cm}^2/\text{s}$ , a value much larger than typical liquid diffusivities. Also, the rate of reaction declined faster than the  $\text{time}^{-1/2}$  dependence predicted by the theory for absorption with an instantaneous reaction.

In one minute's time, complete conversion of all added chlorine to chloride ion was achieved until  $4.7 \times 10^{-4}$  moles of chlorine per  $\text{cm}^2$  of interfacial area had reacted. Subsequent reaction was almost independent of initial chlorine partial pressure.

The amount of chlorine reacted was not sensitive to the rate of oxygen produced by hydrogen peroxide disproportionation. The rate of disproportionation was seen to depend in a complicated manner on the composition of the alkaline solutions.

AFOSR Program Manager: William G. Thorpe, Major, USAF

# COMPLETED PROJECT SUMMARY

1. TITLE: Excited State Chemistry of Halogen Azides
2. PRINCIPAL INVESTIGATOR: Dr. A. T. Pritt, Jr.  
Rockwell International Science Center  
P.O. Box 1085  
Thousand Oaks, CA 91360
3. INCLUSIVE DATES: 1 June 1979 - 31 May 1982
4. CONTRACT NUMBER: F49620-79-C-0053
5. COSTS AND FY SOURCE: \$13,700, FY79; \$66,100, FY80; \$65,800, FY81  
\$46,500, FY82
6. SENIOR RESEARCH PERSONNEL:  
  
Dr. R. D. Coombe (original principal investigator)  
Dr. K. O. Christe  
Dr. F. J. Wodarczyk
7. JUNIOR RESEARCH PERSONNEL:  
  
R. K. Horne  
D. Patel  
D. R. Strauss
8. PUBLICATIONS:  
  
"Azide Mechanisms for the Production of NCl Metastables," A. T. Pritt, Jr. and R. D. Coombe, Int. J. Chem. Kinetics, 12, 741 (1980).  
  
"Visible and Near-Infrared Electronic Transitions in NCl and NBr," A. T. Pritt, Jr., D. Patel, and R. D. Coombe, J. Mol. Spectrosc., 87, 401 (1981).  
  
"Photodissociation of  $\text{ClN}_2$  at 193 and 249 nm," R. D. Coombe, D. Patel, A. T. Pritt, Jr., and F. J. Wodarczyk, J. Chem. Phys., 75, 2177 (1981).  
  
"Decay Kinetics of NCl ( $b^1\Sigma^+, v'$ )," A. T. Pritt, Jr., D. Patel and R. D. Coombe, J. Chem. Phys., 75, 5720 (1981).  
  
"Reaction Rate of F and Cl Atoms with  $\text{HN}_3$ ," A. T. Pritt, Jr. and D. Patel, to be submitted to J. Chem. Phys.  
  
"Rotational Analysis of the O-O Band of the b-X transition in NBr," A. T. Pritt, Jr. and D. Patel, to be submitted to J. Mol. Spectrosc.

## 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The object of this three-year study was to gain an understanding of halogen azides by investigating the photochemistry of these metastable species and by following the reaction kinetics and mechanism associated with the transient intermediate produced in halogen atom-azide radical reactions.

Traditional chemiluminescence flow tube studies were conducted to investigate the kinetics, mechanisms and spectroscopy of flames produced by halogen atom reactions with azide and isocyanate compounds. It had been demonstrated that reactions of  $\text{HN}_3$  with excess fluorine atoms produced  $\text{NF}(a^1\Delta)$  in a two step reaction sequence:  $\text{F} + \text{HN}_3 \rightarrow \text{HF}^\dagger + \text{N}_3$ ;  $\text{F} + \text{N}_3 \rightarrow \text{NF}(a^1\Delta) + \text{N}_2$ . The accompanying  $\text{NF}(b^1\Sigma^+)$  was produced by energy pooling of  $\text{HF}^\dagger$  with  $\text{NF}(a^1\Delta)$ . The reaction of  $\text{F} + \text{ClN}_3$  in which this energy pooling process is not possible produced small quantities of  $\text{NF}(b^1\Sigma^+)$ , indicating that the  $\text{F} + \text{N}_3$  reaction must have an exothermicity of at least 54 kcal/mole. This conclusion assumes that the internal energy carried by the  $\text{N}_3$  radical prior to the reaction is negligible. Substituting excess Cl atoms for F atoms in the  $\text{HN}_3$  reaction produced the  $b^1\Sigma^+$  state consistent with the energetics of the  $\text{Cl} + \text{N}_3$  reaction. The infrared bands in this flame which were confirmed to be the  $a^1\Delta - x^3\Sigma$  transition in  $\text{NCl}$  represent the first spectroscopic evidence of the  $a^1\Delta$  state. Similar observations and conclusions were drawn in the analogous hybrid reaction of F and Br atom reaction with  $\text{HN}_3$ . Spectroscopic constants for the b-X and a-X systems of  $\text{NCl}$  and  $\text{NBr}$  were determined.

A halogen azide intermediate is formed in the halogen atom + azide radical reaction. In an effort to increase our understanding of the nature of these intermediates, a photochemical study of the metastable halogen azides was undertaken. The UV and vacuum UV absorption spectrum of  $\text{ClN}_3$  revealed three distinct absorption features peaking at 250, 205 and  $< 170$  nm similar to that of  $\text{HN}_3$  and  $\text{HNCO}$ ; the major difference in the  $\text{ClN}_3$  absorption was the lack of structure which is present in the hydrogen analog. Pulsed laser photolysis of  $\text{ClN}_3$  at the excimer wavelengths of 193 and 249 nm produced the photofragment,  $\text{NCl}(b^1\Sigma^+)$ . Moreover, from the time resolved laser dissociated fluorescence spectra, a major fraction of the  $\text{NCl}(b^1\Sigma^+)$  is produced with significant vibrational energy up to  $v'=12$ . This high vibrational content is consistent with a Franck-Condon transition in  $\text{ClN}_3$  to a highly repulsive state resulting in rapid departure of the photofragments, leaving the  $\text{NCl}$  with a bond length corresponding to that of the weak  $\text{Cl}-\text{N}_3$  bond. The lack of vibrational excitation in the  $\text{NH}$  photofragment from the photolysis of  $\text{HN}_3$  can be explained in a like manner. Apart from the photo-dissociative spin-allowed channel of producing two products in their singlet states ( $\text{NCl}(b^1\Sigma^+)$  and  $\text{N}_2(X^1\Sigma^+g)$ ), the alternative spin-allowed channel producing two triplet fragments ( $\text{NCl}(X^3\Sigma^-)$  and  $\text{N}_2(A^3\Sigma_u^+)$ ) was also observed albeit indirectly. Addition of NO resulted in the formation of the NO  $\gamma$  band emission which is formed by the fast near resonant energy transfer process from  $\text{N}_2(A^3\Sigma_u^+)$ . The fact that this observation was made for laser photolysis at 249 nm

verifies the metastability of  $\text{ClN}_3$ , with  $\text{ClN}_3$  about  $11,000 \text{ cm}^{-1}$  greater in energy relative to its two separated ground state diatomics  $\text{NCl}-\text{N}_2$ . Furthermore, the energy of  $\text{ClN}_3$  is  $\sim 2000 \text{ cm}^{-1}$  greater in energy than  $\text{NCl}(\text{A}^1 \Delta) + \text{N}_2(\text{X}^1 \Sigma_g^+)$ .

Analysis of vibrationally resolved  $\text{NCl}(\text{b}^1 \Sigma^+)$  quenching rates show that most chaperone gases quench the vibrational manifold faster than electronic quenching out of the  $\text{b}^1 \Sigma^+$  state with the exception of  $\text{ClN}_3$ . Reactive quenching of  $\text{NCl}(\text{b}^1 \Sigma^+)$  by  $\text{ClN}_3$  is a strong function of its vibrational content and it was found that  $\sim 10\%$  of the vibrational energy was utilized in surmounting the activation barrier to reaction. Quenching of  $\text{NCl}(\text{b}^1 \Sigma^+)$  by the halogen halides is relatively fast, suggesting that near resonant E-V energy transfer processes in which the  $\text{b}^1 \Sigma^+$  state is quenched to the  $\text{a}^1 \Delta$  state are operative.

AFOSR Program Manager: William G. Thorpe, Major, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Studies in Non-Equilibrium Statistical Mechanics
2. PRINCIPAL INVESTIGATOR: Professor Herschel Rabitz  
Department of Chemistry  
Princeton University  
Princeton, New Jersey 08544
3. INCLUSIVE DATES: 1 October 1978 - 30 September 1982
4. GRANT NUMBER: AFOSR-78-3724
5. COSTS AND FY SOURCE: \$47,000, FY78; \$59,000, FY79; \$63,655, FY80;  
\$70,000, FY81
6. SENIOR RESEARCH PERSONNEL:  

Dr. Stuart Augustin	Dr. Andrew DePristo
Dr. Jenn-Tai Hwang	Dr. Metin Demiralp
Dr. Samir Saha	
7. JUNIOR RESEARCH PERSONNEL:  

Luis Eslava
Ramakrishna Ramaswamy
Eugene Dougherty
8. PUBLICATIONS:  

"Stochastic Theory for Molecular Collisions: Application to CO-He Systems," R. Ramaswamy, S. Augustin and H. Rabitz, J. Chem. Phys., 70, 2455 (1979).

"On the Correlation of Rotationally Inelastic Rates: A Scaling Theoretical Analysis," R. Ramaswamy, A. DePristo and H. Rabitz, Chem. Phys. Letter., 61, 495 (1979).

"Futher Developments and Applications of the Green's Function Method of Sensitivity Analysis in Chemical Kinetics," E. Dougherty, J. Hwang and H. Rabitz, J. Chem. Phys., 71, 1794 (1979)

"A Scaling Theoretical Analysis of Vibrational Relaxation Experiments: Rotational Effects and Long-Range Collisions," A. DePristo and H. Rabitz, Chem. Phys., 44, 171 (1979).

"Action-Angle Variables in Quantum Mechanics," S. Augustin and H. Rabitz, J. Chem. Phys., 71, 4956 (1979).

"Vibrational and Rotational Collision Processes," A. DePristo and H. Rabitz, Potential Energy Surfaces, A. P. Lawley, ed., (John Wiley and Sons, 1980).



"Computational Kinetics and Sensitivity Analysis of Hydrogen-Oxygen Combustion," E. Dougherty and H. Rabitz, J. Chem. Phys., 72, 6571 (1980).

"Action-Angle Variables for the Quantum Three Particle System," S. Augustin, M. Demiralp, H. Rabitz, and A. Askar, J. Chem. Phys., 73, 268 (1980).

"Stochastic Theory of Intramolecular Energy Transfer in the Presence of Radiation," E. Dougherty, S. Augustin and H. Rabitz, J. Chem. Phys., 74, 1175 (1981).

"Chemical Kinetic Functional Sensitivity Analysis: Elementary Sensitivities," M. Demiralp and H. Rabitz, J. Chem. Phys., 74, 3362 (1981).

"A Rapidly Convergent Expansion Technique for Local Quantum Mechanical Operators," S. Augustin, J. BelBruno, H. Rabitz and H. Gelfand, J. Chem. Phys., 76, 1879 (1982).

"A Localized Integral Equation Formulation of Molecular Scattering," S. Saha and H. Rabitz, J. Chem. Phys., 76, 417 (1982).

"Chemical Sensitivity Analysis Theory with Applications to Molecular Dynamics and Kinetics," H. Rabitz, Computers and Chemistry, 5, 167 (1981).

"A Further Analysis of V-V Transfer Rates for High Lying States of CO," A. DePristo and H. Rabitz, Chem. Phys., 62, 243 (1981).

"Numerical Methods for Solving Time Dependent Quantum Mechanical Problems with Applications," L. Smith S. Augustin and H. Rabitz, J. Comp. Phys., 45, 417 (1982).

"The Initial Value Representation (IVR) for Three-Dimensional Scattering Problems," S. Augustin, J. Chem. Phys., 77, 3953 (1982).

"Scaling Relations for Inelastic Collision Data Obtained from the Initial Value Representation (IVR)," S. Augustin, J. Chem. Phys., 78, 206 (1983).

"Stochastic Theory of Intramolecular Vibrational Energy Redistribution and Dissociation in the Presence of Radiation," L. Eslava, S. Augustin and H. Rabitz, J. Chem. Phys., submitted.

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research was concerned with inter-and intra-molecular dynamics as well as certain aspects of chemical kinetics. An effort was made to approach these problems by developing new tools in order to address questions previously inaccessible. In particular, the research focused on the development and application of three primary topics: (a) stochastic dynamics, (b) sensitivity analysis and (c) collisional scaling theory. Although each of these topics had its own research objective, they are in fact closely related. The research in each area was found to be of

benefit to developments in the other areas. The highlights of these studies are given below.

(a) Stochastic Dynamics. This research aimed at developing a stochastic approach for the dynamics of inter- and intra-molecular motion. The theory was especially designed to treat large complex systems having many quantum levels. The formulation proceeded from Schrodinger's equation by the introduction of an appropriate random phase approximation thereby producing a simpler master equation for the system probabilities. This equation was in turn often approximated by a continuous Fokker-Planck equation producing a physically transparent picture of probability "flowing" amongst the system quantum levels. Appropriate diffusion and convection coefficients could be identified and calculated directly from the original system Hamiltonian, thereby allowing the theory to take on an ab initio form. Calculations were performed on vibrational-rotational inelastic collisions as well as intramolecular energy transfer in the presence of radiation. The theory could be developed further in an ab initio as well as a phenomenological fashion capable of treating large chemical systems.

(b) Sensitivity Analysis. Chemical sensitivity analysis provides a collection of theoretical tools capable of addressing a wide variety of questions in chemical dynamics and chemical kinetics. The research viewed these problems in an input/output perspective and aimed to understand the interrelationship between the system variables. In particular, most physical problems such as in collision dynamics or chemical kinetics have their input information (e.g., the intermolecular potential, rate constants, etc.) parametrically represented. The output is obtained by solving appropriate differential equations, such as Schrodinger's equation or those of chemical kinetics, and sensitivity analysis at its most elementary level aims to understand how the solutions to these equations of motion depend on the parametric input information. These problems are approached from a gradient perspective and more generally an entire family of sensitivity coefficients may be calculated by using the appropriate techniques from multivariable calculus. The research studied problems from collision dynamics as well as chemical kinetics. A publicly available computer code was written for applications in kinetics.

(c) Collisional Scaling Theories. This work concerned the development and application of theoretical techniques primarily to aid the inversion of appropriate laboratory data back to more fundamental information. In particular, bulk relaxation measurements of a spectroscopic nature, such as pressure broadening measurements, are often easy to perform in the laboratory. However, without use of appropriate theoretical insight, such measurements are dynamically too averaged for direct inversion. The scaling theories attempt to provide an a priori relationship between the fundamental cross sections or underlying rate constants responsible for the laboratory observations. In this fashion, the number of fundamental unknowns can be reduced to a level whereby inversions may be achieved. Starting from a sudden approximation, improved scaling theories were produced and applied to the analysis and inversion of spectral line broadening measurements.

AFOSR Program Manager: William G. Thorpe, Major, USAF

# COMPLETED PROJECT SUMMARY

1. TITLE: Computational Study of Nonadiabatic Effects in Atom-Molecule Reactive Scattering

2. PRINCIPAL INVESTIGATOR: Dr. Michael J. Redmon  
Chemical Dynamics Corporation  
1550 W. Henderson Road, Suite N-140  
Columbus, OH 43220

3. INCLUSIVE DATES: 1 April 1981 - 30 September 1982

4. CONTRACT NUMBER: F49620-81-C-0046

5. COSTS AND FY SOURCE: \$50,000, FY81; 50,000, FY82

6. SENIOR RESEARCH PERSONNEL: Dr. B. C. Garrett  
Dr. L. D. Thomas

7. PUBLICATIONS:

"Quenching of the Resonance State of Potassium by Muonium," B. C. Garrett, D. G. Truhlar, and C. F. Melius, Phys. Rev. A, 24, 2853 (1981).

"Solution of the Coupled Equations of Inelastic Atom-Molecule Scattering for a Single Initial State. II. Use of Nondiagonal Matrix Green Functions," L. D. Thomas, J. Chem. Phys., 76, 4925 (1982).

"Analysis of the Resonance in the Three-Dimensional F + H<sub>2</sub> Reaction," R. E. Wyatt, Ber. Bunsenges. Phys. Chem., 86, 437 (1982).

"The Quenching of Na(3<sup>2</sup>P) by H<sub>2</sub>: Interactions and Dynamics," D. G. Truhlar, J. W. Duff, N. C. Blais, J. C. Tully, and B. C. Garrett, J. Chem. Phys., 77, 764 (1982).

"Quantum Dynamics of the Three-Dimensional F + H<sub>2</sub> Reaction I. Energy Distribution and Entropy in the Transition State," J. F. McNutt, R. E. Wyatt, and M. J. Redmon, submitted to J. Phys. Chem.

"Quantum Dynamics of the Three-Dimensional F + H<sub>2</sub> Reaction II. Density and Flux Analysis," J. F. McNutt, R. E. Wyatt, and M. J. Redmon, submitted to J. Phys. Chem.

"Improved Parameterization of Diatomics-in-Molecules Potential Energy Surface for Na(3p<sup>2</sup>P) + H<sub>2</sub> → Na(3s<sup>2</sup>S) + H<sub>2</sub>," N. C. Blais, D. G. Truhlar, and B. C. Garrett, submitted to J. Chem. Phys.

"Quantum Mechanical Differential Reaction Cross Sections for the F+H<sub>2</sub>(v=0) → FH(v'=2)+H Reaction," R. E. Wyatt and M. J. Redmon, submitted to Chem. Phys. Lett.

#### 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The overall objective of an eighteen month research program was to develop theoretical methods for studying nonadiabatic effects in atom-diatomic molecule collisions. A method for computing accurate three-dimensional reactive scattering wavefunctions has been developed. A method for including several electronic states in a molecular scattering calculation has been implemented. An iterative formulation of the exchange kernel approach to reactive scattering has been examined, and is found to have features that warrant its development for problems involving large numbers of coupled equations. A version of the method incorporating finite element techniques has been programmed and preliminary testing has begun on HF-HF self-relaxation. The current code needs refinement and is presently not programmed to allow for reaction. It is anticipated that this approach will allow treatment of several thousand coupled equations on the new generation of supercomputers.

Applications of these numerical methods are being made to several molecular systems, including collisions of atomic sodium, oxygen and fluorine with molecular hydrogen. Angular distributions have been obtained for the fluorine-hydrogen reaction. Quenching probabilities for sodium by hydrogen are providing information on electronic to vibrational energy transfer. Analysis of reactive scattering wavefunctions provides a method for analyzing energy flow during a chemical reaction.

AFOSR Program Manager: William G. Thorpe, Major, USAF

# COMPLETED PROJECT SUMMARY

1. TITLE: Studies of Energy Transfer and Selective Chemical Reaction Using Tunable IR Radiation
2. PRINCIPAL INVESTIGATOR: Dr. Ian W. M. Smith  
The University of Cambridge  
Department of Physical Chemistry  
Cambridge, United Kingdom CBZ 1EP
3. INCLUSIVE DATES: 1 February 1977 - 31 December 1981
4. GRANT NUMBER: AFOSR-77-3240
5. COSTS AND FY SOURCE: \$49,750, FY77; \$15,790, FY78; \$14,956, FY79; \$19,680, FY80; 0, FY81
6. SENIOR RESEARCH PERSONNEL: Dr. Alan Peterson
7. PUBLICATIONS:

"Reactive and Inelastic Collisions involving Molecules in Selected Vibrational States," I.W.M. Smith, Specialist Periodical Reports of the Chemical Society, Reaction Kinetics, Vol 2, Chapter 1, R. J. Donovan, Ed. (1977).

"Reaction and Relaxation of Vibrationally Excited Molecules: A Classical Trajectory Study of Br + HCl ( $v'$ ) and Br + DCl ( $v'$ ) Collisions," I.W.M. Smith, Chem. Phys., 20, 431 (1977).

"Vibrational Relaxation in Atom-Exchange Reactions: Classical Trajectory Calculations on  $H_2(v) + H$  and  $D_2(v) + D$  Collisions on a Realistic Potential," I.W.M. Smith, Chem. Phys. Letters, 47, 219 (1977).

"The Recombination Reaction between Hydroxyl Radicals and Nitrogen Dioxide.  $OH + NO_2 + M (= He, CO_2)$  in the Temperature Range 213-300 K," K. Erler, D. Field, R. Zellner and I.W.M. Smith, Ber. Bunsen. Gesell. Phys. Chem., 81, 22 (1977).

"The Dynamics of Collisions between Vibrationally Excited Diatomic Molecules and Potentially Reactive Atoms," I.W.M. Smith, Ber. Bunsen. Gesell. Phys. Chem., 81, 126 (1977).

"Time-Resolved Vibrational Chemiluminescence : Rate Constants for the Reactions :  $F + HBr$ ,  $HI \rightarrow HF + Br$ ,  $I$  and for the Relaxation of  $HF(v=4)$  and  $HF(v=6)$  by  $HBr$ ,  $HD$ ,  $CO_2$ ,  $N_2O$ ,  $CO$ ,  $N_2$  and  $O_2$ ," I.W.M. Smith and D. J. Wrigley, Chem. Phys., 63, 321 (1981).

Citation Classic : "Quenching of Infrared Chemiluminescence. I. The Rates of Deexcitation of  $CO(4 \leq v \leq 13)$  by  $He$ ,  $CO$ ,  $NO$ ,  $N_2$ ,  $O_2$ ,  $OCS$ ,  $N_2O$  and  $CO_2$ ," G. Hancock and I.W.M. Smith, Current Contents, 21, No. 30, 22 (1981).

"A New Collision Theory for Bimolecular Reactions," I.W.M. Smith, J. Chem. Education, 59, 9 (1982).

"Kinetics of the  $\text{OH} + \text{NO}_2 + \text{M}$  Reaction at High Total Pressures," J. S. Robertshaw and I.W.M. Smith, J. Phys. Chem., 86, 785 (1982).

"Vibrational Photochemistry Using Lasers," I.W.M. Smith, Proceedings of 5th National Quantum Electronics Conference (Wiley, New York, 1982) in press.

"Lasers in the Study of Elementary Processes, I.W.M. Smith, Ber. Bunsenges. Phys. Chem., 86, 395 (1982).

"Direct Rate Measurements on the Reaction :  $\text{D} + \text{OH} \rightarrow \text{OD} + \text{H}$  from 300 K to 515 K," M. J. Howard and I.W.M. Smith, J.C.S. Faraday II, 78, 1403 (1982).

"The Kinetics of Radical-Radical Processes in the Gas-Phase," M. J. Howard and I.W.M. Smith, Prog. React. Kinetics, to be published (1982).

"Vibrational Relaxation of  $\text{HCN}(002)$ ," P. W. Hastings, M. K. Osborn, C. M. Sadowski and I.W.M. Smith, J. Chem. Phys., submitted (1982).

"Lasers and Vibrational Relaxation in Small Molecules," I.W.M. Smith, to be published in Lasers as Reactants and Probes in Chemistry (Plenum, New York, 1982).

"Direct Rate Measurements on the Reactions :  $\text{N} + \text{OH} \rightarrow \text{NO} + \text{H}$  and  $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$ ," M. J. Howard and I.W.M. Smith, Chem. Phys. Letters, 69, 40 (1980).

"Vibrational Energy Transfer from  $\text{CO}(v=1)$ ,  $\text{N}_2(v=1)$ ,  $\text{CO}_2(001)$ ,  $\text{N}_2\text{O}(001)$  and  $\text{OCS}(001)$  to  $\text{O}_3$ , J. S. Robertshaw and I.W.M. Smith, J.C.S. Faraday II, 76, 1354 (1980).

"Time-Resolved Vibrational Chemiluminescence : Rate Constants for the Reaction,  $\text{F} + \text{HCl} \rightarrow \text{HF} + \text{Cl}$ , and for the Relaxation of  $\text{HF}(v=3)$  by  $\text{HCl}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$  and  $\text{O}_2$ , I.W.M. Smith and D. J. Wrigley, Chem. Phys. Letters, 70, 481 (1980).

"Rate Data for :  $\text{O} + \text{OCS} \rightarrow \text{SO} + \text{CO}$  and  $\text{SO} + \text{O}_3 \rightarrow \text{SO}_2 + \text{O}_2$  by a New Time-Resolved Technique," J. S. Robertshaw and I.W.M. Smith, Int. J. Chem. Kinetics, 12, 729 (1980).

"Vibrational Energy Transfer between  $\text{HCN}$  and  $\text{DCN}$  and Hydrogen and Deuterium Halides," G. S. Arnold, R. P. Fernando and I.W.M. Smith, J. Chem. Phys., 73, 2773 (1980).

"Vibrational Relaxation of  $\text{NO}(v=1)$  by Radical Species," R. P. Fernando and I.W.M. Smith, J.C.S. Faraday II, 77, 459 (1981).

"Combining Transition State Theory with Quasiclassical Trajectory Calculations. I : Collinear Collisions," I.W.M. Smith, J.C.S. Faraday II, 77, 747 (1981).

"Vibrational Relaxation of HCN(001) by the Noble Gases, O<sub>2</sub>, N<sub>2</sub> and CO," G. S. Arnold and I.W.M. Smith, J.C.S. Faraday II, 77, 861 (1981).

"Direct Rate Measurements on the Reactions : N + OH → NO + H and O + OH → O<sub>2</sub> + H from 250 K to 515 K," M. J. Howard and I.W.M. Smith, J.C.S. Faraday II, 77, 997 (1981).

"Integrated Intensities For Some Infrared Absorption Bands of HCN," I.W.M. Smith, J.C.S. Faraday II, 77, 2357 (1981).

"Yields of Br\* (4<sup>2</sup>P<sub>1/2</sub>) As A Function of Wavelength in the Photodissociation of Br<sub>2</sub> and IBr," A. B. Peterson and I.W.M. Smith, Chem. Phys., 30, 407 (1978).

"Laser Studies of the Relaxation and Reaction of Species in Defined Quantum States," I.W.M. Smith, Laser-Induced Processes in Molecules, K. L. Kompa and S. D. Smith, eds., (Springer-Verlag, Berlin, 1979).

"Relaxation of HBr(v=1), DBr(v=1) and HCl(v=1) by Bromine Atoms," R. P. Fernando and I.W.M. Smith, J.C.S. Faraday II, 75, 1064, (1979).

"Time-resolved Measurements on the Relaxation of OH(v=1) by NO, NO<sub>2</sub> and O<sub>2</sub>," D. H. Jaffer and I.W.M. Smith, Faraday Discussion Chem. Soc., 67, 212 (1979).

"Chemical Reactions of Vibrationally Excited Molecules," C. B. Moore and I.W.M. Smith, Faraday Discussion Chem. Soc., 67, 146 (1979).

"Relaxation of HCN(001) using Stimulated Electronic Raman Scattering in Cs Vapor as a Tunable Infrared Source," A. B. Peterson and I.W.M. Smith, J. Chem. Phys., 71, 3346 (1979).

Kinetics and Dynamics of Elementary Gas Reactions, I.W.M. Smith, (Butterworths, London and Boston, 1980).

"Chemical Reactions of Selectively Energised Species," I.W.M. Smith, Physical Chemistry of Fast Reactions, Vol 2: Reaction Dynamics, I.W.M. Smith, ed. (Plenum, New York and London, 1980).

"Vibrational Relaxation of NO by Atomic Oxygen," R. P. Fernando and I.W.M. Smith, Chem. Phys. Letters, 66, 218 (1979).

"Chemical Lasers," I.W.M. Smith, Optics and Laser Technology, 12, 77 (1980).

"The Mechanism of the OH + CO Reaction and the Stability of the HOCO Radical," I.W.M. Smith, Chem. Phys. Letters, 49, 112 (1977).

"Quenching of Infrared Chemiluminescence. Part 6 - Rates of Energy Transfer from HF(2 ≤ v ≤ 7) to HF (v = 0), H<sub>2</sub>, D<sub>2</sub> and HD, and from DF(3 ≤ v ≤ 5) to HF(v = 0)," P. R. Poole and I.W.M. Smith, J.C.S. Faraday II, 73, 1434 (1977).

"Quenching of Infrared Chemiluminescence. Part 7 - Rates of Energy Transfer from HF( $2 \leq v \leq 7$ ) and DF( $3 \leq v \leq 5$ ) to a Wide Range of Collision Partners," P. R. Poole and I.W.M. Smith, J.C.S. Faraday II, 73, 1437 (1977).

"Wavelength Dependence of the Branching Ratio for the Production of Br\*( $4^2P_{1/2}$ ) and Br( $4^2P_{3/2}$ ) in the Photolysis of Br<sub>2</sub>," A. B. Petersen and I.W.M. Smith, Lasers in Chemistry, 112 (Elsevier, Amsterdam, 1977).

"Absolute Rate Constants for the Reactions of O( $^3P$ ) Atoms with DCl and DBr," R.D.H. Brown and I.W.M. Smith, Int. J. Chem. Kinetics, 10, 1 (1978).

"Rate Measurements of OH by Resonance Absorption. Part 6 - Rate Constants for OH + NO (+ M)  $\rightarrow$  HNO<sub>2</sub> (+ M) over a Wide Range of Temperature and Pressure," C. Anastasi and I.W.M. Smith, J.C.S. Faraday II, 74, 1056 (1978).

"Flash Photolysis Study of the Spectra of CH<sub>3</sub>O<sub>2</sub> and C(CH<sub>3</sub>)<sub>3</sub>O<sub>2</sub> Radicals and the Kinetics of their Mutual Reactions and with NO," C. Anastasi, I.W.M. Smith and D. A. Parkes, J.C.S. Faraday I, 74, 1693 (1978).

#### 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Tunable infrared lasers have been used to excite selected vibrational levels of molecules for kinetic studies. It was demonstrated that stimulated electronic Raman scattering (SERS) in Cs vapor provides a useful tunable source between 2.7 and 3.3 microns. Later this source was supplanted by an optical parametric oscillator (OPO) supplying high energy pulses (1-5 mJ) over a wider range (1.5-3.6 microns). Both sources have been used in detailed studies of the relaxation of HCN. When finished these experiments will yield the most complete picture of relaxation rates and pathways in any simple polyatomic molecule. In addition, new direct methods have yielded rates of relaxation of (a) high vibrational levels in HF, and (b) NO and OH in collision with other free radicals. Finally, some preliminary work on selective laser-induced chemistry both in the gas-phase and in low temperature matrices has been carried out.

AFOSR Program Manager: William G. Thorpe, Major, USAF



## COMPLETED PROJECT SUMMARY

1. TITLE: Spectroscopy and Chemistry of Molecules with High Vibrational Energy Content
2. PRINCIPAL INVESTIGATOR: Dr. Jeffrey I. Steinfeld  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, MA 02139
3. INCLUSIVE DATES: 1 October 1978 - 30 September 1982
4. GRANT NUMBER: AFOSR-78-3725
5. COSTS AND FY SOURCE: \$61,200, FY78; \$13,500, FY 79; \$52,258, FY80;  
\$80,000, FY81; \$88,031, FY 82
6. SENIOR RESEARCH PERSONNEL:  

Dr. S. Adler-Golden	Dr. T. Anderson
Dr. M. Dubs	Dr. D. S. Frankel
	(Aerodyne Research, Inc.)
7. JUNIOR RESEARCH PERSONNEL:  

J. S. Francisco	M. A. Findeis
M. N. Spencer	R. Goldstein
C. Limoli	
8. PUBLICATIONS:  

"Multiphoton CO<sub>2</sub> Laser Vibrational Heating of the Triplet State of Biacetyl," I. Burak, T. J. Quelly and J. I. Steinfeld, J. Chem. Phys., **70**, 334 (1979).

"Near-Resonant Electronic Energy Transfer from NF ( $a^1\Delta$ ) to Bi," G. A. Capelle, D. G. Sutton and J. I. Steinfeld, J. Chem. Phys., **69**, 5140 (1978).

"Analysis of Perturbations in the  $A^2\Pi-X^2\Sigma^+$  'Red' System of CN," A. J. Kotlar, R. W. Field, J. I. Steinfeld and J. A. Coxon, J. Mol. Spectroscopy, **80**, 86 (1980).

"Microscopic and Macroscopic Analysis of Non-Linear Master Equations: Vibrational Relaxation of Diatomic Molecules," M. Tabor, R. D. Levine, A. Ben-Shaul and J. I. Steinfeld, Mol. Phys., **37**, 141 (1979).

"Surface-Hopping Model for Near-Resonant Electronic Energy Transfer," J. I. Steinfeld and D. G. Sutton, Chem. Phys. Letts., **64**, 550 (1979).

"Energy Deposition in Molecules Resulting from Multiple Infrared Photon Absorption," C. Reiser and J. I. Steinfeld, Opt. Eng., **19**, 2 (1980).

"Formation of Vinylidenecarbene Intermediates in Multiple Infrared Photon Elimination Reactions," C. Rieser and J. I. Steinfeld, J. Phys. Chem., **84**, 680 (1980).

"Laser-Induced Chemical Reactions: Survey of the Literature, 1975-1979," J. I. Steinfeld, in Laser-Induced Chemical Processes, J. I. Steinfeld, Ed., (Plenum Publishing Corp., New York), pp. 243-266 (1980).

"Recent Developments in Laser Photochemistry and Diagnostics," J. I. Steinfeld, Proceedings "Lasers '79" Conference (Orlando, Florida, December 1979).

"Infrared Photochemistry of Cyclobutyl Chloride," J. S. Francisco and J. I. Steinfeld, Intl. J. Chem. Kinetics, **13**, 615 (1981).

"Infrared Photochemistry of bis(Trifluoromethyl) peroxide," J. S. Francisco, J. Findeis and J. I. Steinfeld, Intl. J. Chem. Kinetics, **13**, 627 (1981).

"A Maximum Entropy Model for Branching Ratios in Multiple Infrared Photon Dissociation," W. D. Lawrance, J. Silberstein, Zhang Fu-min, Zhu Qing-shi, J. S. Francisco and J. I. Steinfeld, J. Phys. Chem., **85**, 1961 (1981).

"Chemistry and Spectroscopy of Molecules at High Levels of Excitation," J. I. Steinfeld, to appear in workshop proceedings, "Energy Storage and Redistribution in Molecules", J. Hinze, Ed., (Plenum Publishing Co., New York).

"Convolution and Deconvolution of Focussed Beam Data in Multiphoton Decomposition Experiments," J. S. Francisco, J. I. Steinfeld and R. G. Gilbert, Chem. Phys. Letts., **82**, 311 (1981).

"Very-Low-Pressure Pyrolysis of Chloroethane-2,2,2-d<sub>3</sub>. Kinetics of DCl Elimination and the Effect of CO<sub>2</sub> Inert Bath Gas," J. S. Francisco, J. I. Steinfeld, K. D. King and R. G. Gilbert, J. Phys. Chem., **85**, 4106 (1981).

"Influence of Collisions on Coherent IR Multiphoton Absorption in Thiophosgene," D. M. Brenner, M. Spencer and J. I. Steinfeld, J. Chem. Phys., **75**, 3153 (1981).

"Infrared Multiphoton Decomposition and Energy-Dependent Absorption Cross Section of Chloroethane," J. S. Francisco, W. D. Lawrance, J. I. Steinfeld and R. G. Gilbert, J. Phys. Chem., **86**, 724 (1982).

"Vibrational Analysis of Chloroethane-2-d<sub>1</sub>," J. S. Francisco, Zhu Qingshi and J. I. Steinfeld, Spectrochim Acta., **38A**, 671 (1982).

"Diode Laser Spectroscopy of the  $\nu_9$  Band of Ethyl Chloride," Zhu Qingshi, J. S. Francisco and J. I. Steinfeld, J. Mol. Spectroscopy, **92**, 257 (1982).

"Multiple Infrared Photon Dissociation and Kinetics of  $\text{CF}_3\text{O}$  Radicals," Zhang Fu-min, J. S. Francisco and J. I. Steinfeld, J. Phys. Chem., **86**, 2402 (1982).

"Chemical Laser Operation and n-Butane Absorption Coefficient at DF R-branch Lines," D. Frankel and S. L. Frankel, Appl. Opt., **21**, 718 (1982).

"Infrared Multiphoton Absorption Dynamics in Chloroethane Molecules," J. S. Francisco, Zhu Qingshi, J. I. Steinfeld and R. G. Gilbert, Proc. XIIth Intl. Quantum Electronics Conf. (Munich), Appl. Phys., **B28**, 184 (1982).

"Photophysics of Infrared Multiphoton Excitation in Thiophosgene," D. M. Brenner, M. N. Spencer and J. I. Steinfeld, J. Chem. Phys., in press.

"Infrared Multiphoton Decomposition and Energy-Dependent Absorption Cross Sections of Chloroethane- $\text{d}_0$ , -2- $\text{d}_1$ , and -2,2,2- $\text{d}_3$ ," J. S. Francisco, Zhu Qingshi and J. I. Steinfeld, submitted to J. Chem. Phys.

"Spectroscopy and Chemistry of Molecules with High Vibrational Energy Content," J. I. Steinfeld, Final Technical Report.

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The overall objectives in this program were to characterize the reactivity, spectroscopy, and dynamics of vibrationally excited small polyatomic molecules. The reactivity of a variety of molecules excited to dissociation by infrared multiple-photon absorption (IRMPA) has been investigated. The species  $\text{R}_2\text{C}=\text{CHCl}$  ( $\text{R} = \text{CH}_3, \text{F}$ ) were found to produce the vinylidenecarbene intermediate,  $\text{R}_2\text{C} = \text{C}:$ , which rearranged to the substituted acetylene except in the case of  $\text{R} = \text{F}$ , where the rearrangement was hindered. The species  $\text{C}_4\text{H}_7\text{Cl}$  (cyclobutyl chloride) was found to possess three competitive dissociation channels, viz.,  $\text{HCl}$  elimination, ring scission, and  $\text{C}=\text{Cl}$  homolysis. The species  $\text{CF}_3\text{OOCF}_3$  (bis(trifluoromethyl)peroxide) was dissociated by cleavage of the  $\text{O}-\text{O}$  bond; the resulting  $\text{CF}_3\text{O}$  radicals underwent secondary dissociation to  $\text{CF}_2\text{O} + \text{F}$ . The most extensive series of investigations was carried out on normal ( $-\text{d}_0$ ) and deuterated ( $-2-\text{d}_1$ ,  $-2,2,2-\text{d}_3$ ) chloroethane. By the use of a Master-Equation model, we were able to estimate the energy-dependent infrared absorption cross-section  $\sigma(E)$ ; both increasing deuteration and increasing energy within the molecule have the effect of enhancing the statistical behavior of  $\sigma(E)$ . Spectroscopic and kinetic investigations were also carried out on these molecules.

Infrared-optical double-resonance methods have been employed to probe the excitation dynamics and distributions in IRMPA. In a collaboration with Dr. D. Brenner of the Brookhaven National Laboratory, vibrational levels of thiophosgene were probed by laser-induced fluorescence excitation spectroscopy under both collision-free (beam) and bulk-gas conditions. The dominant feature in this system appears to be highly efficient on-resonant pumping of very weak overtone and combination bands; the most astonishing result is the apparently huge effect of collisions in suppressing this pumping process. We are also developing a Coherent Anti-Stokes Raman method for probing vibrational distributions following IRMPA.

Towards the conclusion of the present research grant, increasing emphasis was placed on laser-initiated reactions taking place at or near surfaces, particularly of fluorocarbon radicals generated by IRMPA with silicon surfaces. Optical diagnostic techniques, particularly laser-induced fluorescence, have been developed for studying these reactions, and work is now proceeding along these lines.

We also attempted to investigate the reactivity of single-photon-excited molecules, using a DF chemical laser oscillating at  $3.4\text{ }\mu\text{m}$  to excite C-H stretching modes in alkanes. Although laser operation at these wavelengths was achieved, and excitation cross-sections measured, difficulties with sample purity and analytical procedures prevented us from obtaining a definitive result in this particular area.

AFOSR Program Manager: William G. Thorpe, Major, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Radiation and Laser Potential of Homo and Heteronuclear Rare-gas Diatomic Molecules

2. PRINCIPAL INVESTIGATORS:

W. C. Walker  
Department of Physics  
University of California  
Santa Barbara, CA 93106

Yoshio Tanaka  
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Santa Barbara, CA 93106

3. INCLUSIVE DATES: 30 September 1976 - 31 October 1982

4. GRANT NUMBER: AFOSR-77-3137

5. COSTS AND FY SOURCE: \$54,077, FY77; \$54,335, FY78; \$57,685, FY79;  
\$51,941, FY80; \$51,600, FY81

6. JUNIOR PERSONNEL:

W. Spates  
Zenglie Wu

E. Smith  
B. Zacher

7. PUBLICATIONS:

"Emission Spectrum of Rare-Gas Dimers in the Vacuum Ultraviolet, I. Ar<sub>2</sub>," Y. Tanaka, W. C. Walker and K. Yoshino, J. Chem. Phys., 70, 380 (1979).

"Emission Spectrum of Rare-gas Dimers in the Vacuum Ultraviolet, II. Rotational Analysis of Band System I of Ar<sub>2</sub>," D. E. Freeman, K. Yoshino and Y. Tanaka, J. Chem. Phys., 71, 1780 (1980).

"Emission Spectrum of Rare-Gas Dimers in the Vacuum Ultraviolet, III. Ne<sub>2</sub>," Y. Tanaka and W. C. Walker, J. Chem. Phys., 74, 2760 (1981).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research consisted of a study of the emission spectra of the rare-gas dimers Ne<sub>2</sub>, Ar<sub>2</sub>, and Kr<sub>2</sub> in the region 500-2000 Å. The aim of the research was to discover new band systems, identify their origin and determine excited state energies and molecular constants. Band systems associated with the transition from states  $^3\Sigma_g^+$ ,  $^1\Sigma_g^+$ , and B 5p  $\sigma(Ou^+)$  to the ground state  $X^1\Sigma_g^+$  of the Ar<sub>2</sub> dimers were observed in the region 1074-1300 Å. A rotational analysis of the band yielded rotational constants B<sub>v</sub> and D<sub>v</sub> for the state  $^3\Sigma_g^+$  as follows:

$B_{v+1} = 0.055 \text{ cm}^{-1}$  to  $B_{v-6} = 0.1051 \text{ cm}^{-1}$  and  $D_{v+1} = 1.0 \times 10^{-6}$  to  $D_{v-6} = 0.3 \times 10^{-6} \text{ cm}^{-1}$ . The analysis indicated that the coupling scheme for the lowest excited state is closer to Hunds case b than to case c.

For  $\text{Ne}_2$  band systems were observed from the states  $1_u(^3P_2)$  and  $0_u^+(^3P_1)$  to the  $X \ 0_g^+(^1S_0)$  ground states as well as band due to  $0_u^+(^1P_1) \rightarrow 0_g^+(^1S_0)$ . A dissociation energy of  $544 \text{ cm}^{-1}$  was obtained for the  $0_u^+(^1P_1)$  state. One new band system in the range  $779\text{--}792 \text{ \AA}$  was observed as well as a new continuum near  $800\text{--}880 \text{ \AA}$  were observed. Detailed analysis of the band originating from  $0_u(^3P_1)$  allowed us to deduce a "hump" in the potential curve of this state at large interatomic radii. The "hump" height found was  $670.5 \text{ cm}^{-1}$  which is considerably smaller by a factor of six than that calculated by Cohen and Schneider.

Spectra for  $\text{Kr}_2$  were recorded in the range  $1100\text{--}1500 \text{ \AA}$  for a variety of excitations and many pressures. Band systems involving transitions to the states  $X \ 1_{\Sigma_g^+}$  and  $X \ 1_{\Sigma_g^-}$  from states  $1_u$  and  $0_u$  were studied. The  $0_u$  excited state was determined to be stable with a dissociation energy  $D_0 = 441.8 \text{ cm}^{-1}$ .

AFOSR Program Manager: William G. Thorpe, Major, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Kinetic Studies of Gas Phase Free Radicals
2. PRINCIPAL INVESTIGATOR: Dr. Curt Wittig  
Departments of EE, Physics and Chemistry  
University of Southern California  
University Park, MC 0484  
Los Angeles, CA 90089
3. INCLUSIVE DATES: 1 October 1978 - 30 September 1982
4. GRANT NUMBER: AFOSR-78-3693
5. COST AND FY SOURCE: \$83,607, FY78; \$94,278, FY79; \$70,000, FY80;  
\$77,000, FY81

6. SENIOR RESEARCH PERSONNEL:

Dr. H. Reisler  
Dr. M. S. Mangir  
Dr. A. M. Renlund

Dr. F. Kong  
Dr. Y. Haas  
Dr. F.B.T. Pessine

7. JUNIOR RESEARCH PERSONNEL:

Dr. M. H. Yu  
Ms. F. Shokoohi

8. PUBLICATIONS:

"Collisionless Production of Electronically Excited Species via IR Laser Photolysis," M. H. Yu, H. Reisler, M. Mangir, and C. Wittig, Chem. Phys. Letter, **62**, 439 (1978).

"The Kinetics of Free Radicals Generated by IR Laser Photolysis: I. Reactions of  $C_2(a^3\Pi_u)$  with NO, Vinyl Cyanide and Ethylene," H. Reisler, M. Mangir, and C. Wittig, J. Chem. Phys., **71**, 2109 (1979).

"The Kinetics of Free Radicals Generated by IR Laser Photolysis: II. Reactions of  $C_2(a^3\Pi_u)$ ,  $C_2(X^1\Sigma_g^+)$ ,  $C_3(X^1\Sigma)$ , and  $CN(X^2\Sigma^+)$  Radicals with Oxygen," H. Reisler, M. Mangir, and C. Wittig, Chem. Phys., **47**, 49 (1980).

"The Kinetics of Free Radicals Generated by IR Laser Photolysis: III. Intersystem Crossings Between  $C_2(X^1\Sigma_g^+)$  and  $C_2(a^3\Pi_u)$  Induced by Oxygen," M. S. Mangir, H. Reisler, and C. Wittig, J. Chem. Phys., **73**, 829 (1980).

"The Kinetics of Free Radicals Generated by IR Laser Photolysis: IV. Intersystem Crossings and Reactions of  $C_2(X^1\Sigma_g^+)$  and  $C_2(a^3\Pi_u)$  in the Gaseous Phase," H. Reisler, M. S. Mangir, and C. Wittig, J. Chem. Phys., **73**, 2280 (1980).

"Luminescence of Radicals Resulting from IR Multiple Photon Excitation," H. Reisler and C. Wittig, Photoselective Chemistry, J. Jortner, R. D. Levine, and S. A. Rice, eds., Advance Chem. Phys. Series, Part I, 679 (1981).

"IR Laser Photolysis of Polyatomic Molecules: A Powerful Technique for Studying Elementary Processes in the Gas Phase," M. R. Levy, H. Reisler, M. Mangir, and C. Wittig, Optical Engineering, 19, 29 (1980).

"Laser Kinetic Spectroscopy of Elementary Processes," H. Reisler, M. S. Mangir, and C. Wittig, Chemical and Biochemical Applications of Lasers, Vol. V., C. B. Moore, ed, 139 (1980).

"Intramolecular Processes in Isolated Polyatomic Molecules," M. R. Levy, A. M. Renlund, H. Reisler, M. S. Mangir, T. Watson, and C. Wittig, How Stationary are Molecular States, J. Hinze, ed., (Plenum), in press.

"The Unimolecular Reaction of Isolated  $\text{CF}_3\text{CN}$ : Energy Disposal into CN Product Degrees of Freedom," H. Reisler, F. Kong, A. Renlund, and C. Wittig, J. Chem. Phys., 76, 997 (1982).

"The Unimolecular Reaction of Isolated  $\text{CF}_3\text{CN}$ : The Influence of Laser Fluence/Intensity on the Rovibronic Excitation of CN Produced via Infrared Multiple Photon Dissociation," H. Reisler, F. Kong, C. Wittig, J. Stone, E. Thiele, and M. F. Goodman, J. Chem. Phys., 77, 328 (1982).

"Gas Phase Reactions of  $\text{C}_2\text{H}(\text{X}^2\Sigma^+)$  with  $\text{O}_2$ ,  $\text{H}_2$ , and  $\text{CH}_4$ ," A. M. Renlund, F. Shokoohi, H. Reisler, and C. Wittig, Chem. Phys. Lett., 84, 293 (1981).

"The Reaction of  $\text{C}_2\text{H}$  with  $\text{O}_2$ : Chemiluminescent Products," A. Renlund, F. Shokoohi, H. Reisler, and C. Wittig, J. Phys. Chem., 86, 4165 (1982).

"The Unimolecular Reaction of  $(\text{CH}_3)_3\text{CNO}$  following  $n-\pi^*$  Excitation with a Tunable Dye Laser," H. Reisler, F. B. T. Pessine, Y. Haas, and C. Wittig, J. Chem. Phys., in press.

"Reactions of  $\text{C}_2\text{H}$  with Small Molecules," F. Shokoohi, T. Watson, H. Reisler, and Wittig, in preparation.

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

Our research in the past four years was concerned with the study of uni- and bimolecular elementary processes in the gas phase using laser kinetic and spectroscopic techniques. Our objective was to study in detail reactions of small free radicals which are representative of broader classes of reactions. More recently, these studies were extended to include also unimolecular reactions of simple molecules with emphasis on detailed energy distributions among the various degrees of freedom of the products.



The excitation and diagnostic methods that we employed offer the required time resolution to directly measure unimolecular and bimolecular reaction rates, and the spectral resolution to derive accurate energy distributions among the various degrees of freedom of the products. We used IR, UV, and visible lasers for photolysis, and laser induced fluorescence (LIF), chemiluminescence, and multiphoton ionization (MPI) for detection. These methods offer excellent temporal and spectral resolution, as well as high sensitivity and selectivity.

Our studies of bimolecular reactions have been concerned with state specific reactions of  $C_2$ ,  $C_3$ , and  $C_2H$  radicals, which are important in combustion, air pollution, astrophysics, and the chemistry of the upper atmosphere. The rate coefficients and mechanisms of reactions of these radicals were largely unknown when we initiated our studies. Today, we have a fairly complete picture of numerous reactions, whereas some, most notably reactions of  $C_2H$  radicals in their ground electronic state, still await good diagnostics.

We have demonstrated that the room temperature chemistry of  $C_2(X^1\Sigma_g^+)$  is strikingly different than that of  $C_2(a^3\Pi_u)$  (hereafter referred to as  $^1C_2$  and  $^3C_2$  respectively). In reactions of  $^1,^3C_2$  with  $NO$  and  $O_2$  we observed a high degree of specificity regarding both reactants and products, and have determined the energy disposal and branching ratios in some of the products. In reactions with hydrocarbons, our results suggest that  $^1C_2$  and  $^3C_2$  are removed mainly via chemical reactions. However,  $^1C_2$  reacts more rapidly than  $^3C_2$  for every case that we have measured. These results were explained by using molecular orbital symmetry considerations.

In addition to looking at reactive channels, we have also studied the intersystem crossing between  $^1C_2$  and  $^3C_2$  induced by atoms and molecules. We find that intersystem crossing is significant only when it is spin allowed (e.g.  $O_2$ ), or involves heavy collision partners (e.g.  $Kr$ ,  $Xe$ ).

In our studies of the  $C_2H$  radicals we employed its chemiluminescent reaction with  $O_2$  as a diagnostic. We find that the reactant is most likely excited  $C_2H$  in the  $A^2\Pi$  state which lies only  $3700\text{ cm}^{-1}$  above the ground state, and thus the rates that we measure are the sum of the quenching and reactive rates. We also find in the reaction with  $O_2$  that products are observed which derive from motion along different potential surfaces and require specific nuclear configurations.

Our studies of unimolecular reactions are concerned with simple bond fission reactions. We attempt to determine both the dissociation rate and energy disposal among reaction products. We have studied the unimolecular reaction of  $CF_3CN$  induced by infrared multiple photon excitation. We find that the rotational, translational, and vibrational temperatures in the  $CN$  fragment are different, and that modified statistical theories are required to explain our results. In addition, we find that both the dissociation rate and the internal energy in the products vary with the  $CO_2$  laser fluence/intensity.

Finally, we studied the unimolecular reaction of  $(\text{CH}_3)_3\text{CNO}$  following  $n-\pi^*$  excitation with a tunable dye laser. We find that the NO production rate was  $> 10^8 \text{ s}^{-1}$  at 570-710 nm, and this rate is too fast to be consistent with a mechanism involving a radiationless transition to the ground electronic state.

AFOSR Program Manager: William G. Thorpe, Major, USAF

RESEARCH EFFORTS COMPLETED IN FY82

CHEMICAL REACTIVITY AND SYNTHESIS - DR. ANTHONY J. MATUSZKO

New Laser Dye Systems Based on  
Transition Metal Complexes  
AFOSR-78-3590

James N. Demas  
Department of Chemistry  
University of Virginia  
Charlottesville, VA 22901

Synthesis and Evaluation of New  
Intramolecular Cure Inter-  
mediates  
AFOSR-82-0140

William A. Feld  
Department of Chemistry  
Wright State University  
Dayton, OH 45435

Exploratory High Pressure  
Chemistry  
AFOSR-79-0092

John Gladysz  
Department of Chemistry  
University of California,  
Los Angeles  
Los Angeles, CA 90024

Synthesis and Characterization of  
Transition Metal Complex Systems  
with Novel Solid State Properties  
F49620-79-C-0051

L. V. Interrante  
General Electric Company  
Corporate Research and  
Development  
Schenectady, NY 12301

Synthesis of Novel Fluorine  
Compounds: New Experimental  
Challenges in Elemental Fluorine  
Chemistry  
AFOSR-78-3658

Richard J. Lagow  
Department of Chemistry  
The University of Texas  
Austin  
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Fabricable Polymers for Matrices  
and Adhesives Which Are Extremely  
Stable to Heat, Oxidation, and  
Hydrolysis  
AFOSR-77-3112

Carl S. Marvel  
Department of Chemistry  
University of Arizona  
Tucson, AZ 85721

Synthesis of Phosphotriazines for  
Potential High Temperature Fluids  
and Elastomers Application  
F49620-79-C-0037

K. L. Paciorek  
Ultrasystems, Inc.  
2400 Michelson Drive  
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Study of the Interaction of  
Hydrazine, Methylhydrazine, and  
Unsym-Dimethylhydrazine with  
Porphyrins, Metalloporphyrins  
and Some Metal Coordination  
Compounds  
AFOSR-82-0137

Albert N. Thompson, Jr.  
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Spelman College  
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Organosilicon Compounds and  
Organosilicon Polymer  
Intermediates  
AFOSR-79-0007

Dietmar Seyferth  
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Chemical Reactions and Properties  
of Organosilicon Compounds Related  
to New Materials  
AFOSR-78-3750

Robert West  
Department of Chemistry  
University of Wisconsin  
Madison, WI 53706

# COMPLETED PROJECT SUMMARY

1. TITLE: New Laser Dye Systems Based on Transition Metal Complexes
2. PRINCIPAL INVESTIGATOR: Dr. James N. Demas  
Department of Chemistry  
University of Virginia  
Charlottesville, VA 22901
3. INCLUSIVE DATES: 1 June 1978 - 31 May 1982
4. GRANT NUMBER: AFOSR-78-3590
5. COSTS AND FY SOURCE: \$35,000, FY78; \$35,000, FY79; \$35,000, FY80;  
\$35,000, FY81

6. SENIOR RESEARCH PERSONNEL:

Dr. S. H. Peterson  
Dr. W. P. Krug  
Dr. W. Dressick

Dr. K. Mandal  
Dr. B. Hauenstein

7. JUNIOR RESEARCH PERSONNEL:

Graduate Students:

D. G. Taylor  
S. Buell  
B. Carraway

T. J. Turley  
T. D. L. Pearson  
S. Snyder

Undergraduates:

M. Greer  
E. Cetron  
J. Toney

F. W. Reed  
J. Love  
J. Cline, Jr.

8. PUBLICATIONS:

"Reversible Excited-State Electron-Transfer Reactions of Transition Metal Complexes," B. A. DeGraff, J. N. Demas, and D. G. Taylor, Solar Energy Conversion and Storage, Ed. by R. B. King, C. R. Kutal, and R. R. Hautala, The Humana Press, Clifton, N.J., 189 (1979).

"Light-Intensity Measurements I. Large Area Bolometers with Microwatt Sensitivities and Absolute Calibration of the Rhodamine B Quantum Counters," D. G. Taylor and J. N. Demas, Anal. Chem., 51, 712 (1979).

"Light Intensity Measurements II. Luminescent Quantum Counter Comparator and Evaluation of Some Luminescent Quantum Counters," D. G. Taylor and J. N. Demas, Anal. Chem., 51, 717 (1979).

"The Step Excitation Method for Studying Reversible Excited-State Electron-Transfer Reactions: Experimental Realization," D. G. Taylor and J. N. Demas, J. Chem. Phys., 71, 1032 (1979).

"Charge Transfer Luminescence from an  $\alpha$ -Diimine Complex of Ruthenium(II)," W. P. Krug and J. N. Demas, J. Am. Chem. Soc., 101, 4394 (1979).

"Excited-State Acid-Base Reactions of Dicyanobis(2,2'-bipyridine)ruthenium(II) and Dicyanobis(1,10-phenanthroline)ruthenium(II)," J. Am. Chem. Soc., 101, 6571 (1979).

"On the Intersystem Crossing Yields of Ruthenium(II) and Osmium(II) Photosensitizers," D. G. Taylor and J. N. Demas, Inorg. Chem., 18, 3177 (1979).

"On the Measurement of Luminescence Risetimes. A Case Study of the Risetimes of Rhodium(III) Complexes," S. H. Peterson, J. N. Demas, T. Kennelly, H. Gafney, and D. P. Novak, J. Phys. Chem., 83, 2991 (1979).

"A Microcomputer Controlled Boxcar Integrator with Subnanosecond Risettime," D. G. Taylor, T. J. Turley, M. Rodgers, S. H. Peterson, and J. N. Demas, Rev. Sci. Instrum., 51, 855 (1980).

"A Microcomputer Interfaced Spectrophotometer for Kinetic Analysis," C. S. Nichols, J. N. Demas, T. H. Cromartie, Anal. Chem., 52, 205 (1980).

"A Microcomputerized Text Editor for Scientific and Chemical Manuscripts," J. N. Demas and S. E. Demas, J. Chem. Ed., 57, 252 (1980).

"Singlet Energy Transfer from the Charge Transfer Excited State of Tris (2,2'-bipyridine)ruthenium(II)," K. Mandal, T. D. L. Pearson, and J. N. Demas, J. Chem. Phys., 75, 2507 (1980).

"An Analysis of Errors in the Phase Plane Method of Deconvolution of Luminescence Lifetimes," F. W. Reed and J. N. Demas, NATO Advanced Study Institute Series, Time Resolved Spectroscopy, in press.

"Luminescent Quantum Counters Based on Organic Dyes in Polymer Matrices," K. Mandal, T. D. L. Pearson, and J. N. Demas, Anal. Chem., 52, 2184 (1980).

"New Luminescent Quantum Counter Systems Based on a Transition Metal Complex," K. Mandal, T. D. L. Pearson, and J. N. Demas, Inorg. Chem., 20, 786 (1981).

"Determination of the Quantum Yield of the Ferrioxalate Actinometer with Electrically Calibrated Radiometers," J. N. Demas, W. D. Bowman, E. F. Zalewski, and R. A. Velapoldi, J. Phys. Chem., 85, 2766 (1981).

"Evaluation of Errors in the Phase Plane Method for Deconvolution of Luminescence Lifetime Data," J. M. Greer, F. W. Reed, and J. N. Demas, Anal. Chem., 53, 710 (1981).

"Surfactant Enhanced Singlet Energy Transfer from the Charge Transfer Excited State of Tris(2,2'-bipyridine)ruthenium(II)," K. Mandal and J. N. Demas, Chem. Phys. Lett., 84, 410 (1981).

"A Program for the Preparation of Posters and Overhead Transparencies," T. D. L. Pearson, M. J. Greer, and J. N. Demas, J. Chem. Ed., 58, 691 (1981).

"Low Frequency Computerized Lock-In Amplifier," J. Toney and J. N. Demas, Rev. Sci. Instrum., 53, 1082 (1982).

"Low Cost Temperature Controller," S. Buell and J. N. Demas, Anal. Chem., 54, 1214 (1982).

"The Measurement of Photon Yields," J. N. Demas, in Photoluminescence Spectrometry, Ed. K. D. Mielenz, Academic Press, 195 (1982).

"A Simple Cell for Deoxygenation of Surfactant Containing Solutions," S. Buell and J. N. Demas, Rev. Sci. Instrum., in press.

"A Simple High Yield Preparation of Tris(oxalato)iridate(III) with a Novel Solvent Extraction Step," C. M. Flynn, Jr., and J. N. Demas, Inorg. Chem. Acta (Lett.), in press.

"An Axes Drawing Program for the 9872A and 7225A Digital Plotters," T. D. L. Pearson and J. N. Demas, J. Chem. Ed., accepted.

"An Autozeroing Microcomputerized Boxcar Integrator," T. D. L. Pearson, J. N. Demas, and S. Davis, Anal. Chem., accepted.

"Singlet Energy Transfer from the Charge Transfer Excited State of Tris(2,2'-bipyridine) ruthenium (II) to Laser Dyes," K. Mandal, T. D. L. Pearson, W. P. Krug, and J. N. Demas, J. Am. Chem. Soc., accepted.

"Heterogeneous Preparation of Singlet Oxygen Using an Ion-Exchange Bound Tris (2,2'-bipyridine) ruthenium(II) Photosensitizer," S. Buell and J. N. Demas, submitted.

"Interactions of Ruthenium(II) Photosensitizers with Triton X-100 Surfactant," K. Mandal, B. L. Hauenstein, Jr., J. N. Demas and B. A. DeGraff, submitted.

"Electron Transfer Quenching of Ruthenium(II) Photosensitizers by Mercury(II) Chlorides. I. Reactions in Aqueous Solution," B. L. Hauenstein, Jr., K. Mandal, J. N. Demas, and B. A. DeGraff, submitted.

"Electron Transfer Quenching of Ruthenium(II) Photosensitizers by Mercury(II) Chlorides. II. Reactions in Aqueous Sodium Lauryl Sulfate Micellar Solutions," W. J. Dressick, B. L. Hauenstein, Jr., J. N. Demas, and B. A. DeGraff, submitted.

"Excited State Lifetime Measurements: Linearization of the Forster Equation by the Phase Plane Method," J. C. Love and J. N. Demas, submitted.

"New Laser Dye Systems BASED on Transition Metal Complexes," James N. Demas, Final Technical Report.

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Major goals of this study have been the elucidation of the photochemical and photophysical processes of platinum metal complexes. While no new laser dye systems have been developed, the fundamental studies necessary to develop binary laser dye systems have been completed. The work has also led to a further understanding of the excited state processes in Ru(II) photosensitizers and to the development of a variety of new chemical systems.

Contrary to the widely-held view that the charge transfer (CT) excited states of Ru(II) complexes, are triplet states, it was demonstrated experimentally that they possess a great deal of singlet character. This has been shown using diffusional singlet energy transfer to the singlet states of laser dyes. This result also shows that the metal complexes can potentially be used as energy antenna in binary laser dye systems. Very efficient micellar-enhanced singlet energy transfer has also been demonstrated. Models for the binding of Ru(II) photosensitizers to nonionic surfactants were developed. Charge surfactants have been used to impede quenching and electron transfer reactions.

Polymer supported tris(2,2'-bipyridine)ruthenium(II) has also been studied as a heterogeneous singlet oxygen generator. A model of the structure of the binding sites and the routes by which singlet oxygen reactions occur in these systems has been developed.

There was a widely held view that fully ring aromatized polypyridine ligands were required with platinum metal complexes to yield CT photosensitizers. Dr. Demas and his coworkers demonstrated that only the  $\alpha$ -diimine functionality need be present for CT luminescence. This opens up an entirely new class of CT excited state photosensitizers.

The first example of an excited state acid base reaction of a complex exhibiting CT luminescence was reported. A unique inversion of the lowest state was observed on protonation. On protonation the CT state rose above the lowest  $\pi - \pi^*$  triplet state, and the emission changed from a CT one to a  $\pi - \pi^*$  phosphorescence.

A variety of new tools and techniques was developed. These include mathematical and instrumental methods of luminescence lifetime analysis, calibration of chemical actinometers, new luminescence quantum counter systems based on solid polymer matrices and/or metal complexes, and new methods of studying fast reversible excited state electron transfer reactions. Also developed were a low-cost temperature controller, a rapid surfactant deoxygenation system, and useful computer programs.

AFOSR Program Manager: Dr. Anthony J. Matuszko



## COMPLETED PROJECT SUMMARY

1. TITLE: Synthesis and Evaluation of New Intramolecular Cure Intermediates

2. PRINCIPAL INVESTIGATOR: Dr. William A. Feld  
Department of Chemistry  
Wright State University  
Dayton, Oh 45435

3. INCLUSIVE DATES: 1 April 1982 - 30 September 1982

4. GRANT NUMBER: AFOSR-82-Q140

5. COSTS AND FY SOURCE: \$9,996, FY82 (Minigrant)

6. JUNIOR RESEARCH PERSONNEL: Stefan A. Babirad

7. PUBLICATIONS:

"Synthesis and Evaluation of New Intramolecular Cure Intermediates,"  
W. A. Feld, Final Technical Report.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives of this research were the syntheses of 1,4,4,7-tetraphenylhepta-1,6-diyne-3,5-dione, 1,3,4,6-tetraphenylhexa-3-ene-1,5-diyne, 3-amino-2-(m-aminophenylethynyl)-N-phenylbenzamide and 4-amino-2-(m-aminophenyl-ethynyl)-N-phenylbenzamide and their evaluation as potential intramolecular cure (IMC) agents.

The reaction of diphenylmalonyl dichloride with phenylacetylene in the presence of bis(triphenylphosphine)palladium(II)dichloride yields diphenylbutadiyne as the major product. The reaction of similarly substituted malonyl dichlorides with cuprous phenylacetylide yields only diphenylbutadiyne. The reaction of phenylethynylmagnesium bromide with substituted malonaldehydes followed by oxidation of the resulting diol to a diketone represents a better synthetic method if the malonaldehydes are available.

The reaction of 1,2-dibromo-1,2-diphenylethene or 1,2-diiodo-1,2-diphenylethene with phenylacetylene using bis(triphenylphosphine)palladium(II)dichloride as a catalyst or with cuprous phenylacetylide yields a mixture of diphenylacetylene and diphenylbutadiyne. The reaction of 3-bromo-1,3-diphenyl-propyne with potassium tert-butoxide provided a highly fluorescent hydrocarbon which exhibits a DSC exotherm at 220°C (maximum) following a melt at 154°C. Characterization is incomplete.

Nitration of o-iodobenzoic acid provided 5-nitro-2-iodobenzoic acid which was converted smoothly to the N-phenylamide. Diazotization of 2-amino-4-nitro-benzoic acid provided 4-nitro-2-iodobenzoic acid which was

also smoothly converted to the N-phenylamide. Coupling reactions of either of the above mentioned iodo compounds with m-aminophenylacetylene are anticipated to give the desired products.

AFOSR Program Manager: Dr. Anthony J. Matuszko

## COMPLETED PROJECT SUMMARY

1. TITLE: Exploratory High Pressure Chemistry
2. PRINCIPAL INVESTIGATOR: Dr. John Gladysz  
Department of Chemistry  
University of California, Los Angeles  
Los Angeles, CA 90024
3. INCLUSIVE DATES: 1 April 1979 - 31 March 1982
4. GRANT NUMBER: AFOSR-79-0092
5. COSTS AND FY SOURCE: \$27,135, FY79; \$30,477, FY80; \$31,000, FY81
6. SENIOR RESEARCH PERSONNEL: Dr. Bong-Rae Cho
7. JUNIOR RESEARCH PERSONNEL:

Wilfried Krone-Schmidt  
David Parker  
Ron Ugolick

Yeung Yu  
Jim Tomasello  
Sung Lee

### 8. PUBLICATIONS:

"High-Pressure Cycloadditions of Pyrones; Synthesis of Highly Functionalized Six-Membered Rings by Inhibition of Carbon Dioxide Loss," J. A. Gladysz, S. J. Lee, J. A. V. Tomasello, and Y. S. Yu, J. Org. Chem., **42**, 4179 (1977).

"Ene Reactions of  $\beta$ -Pinene at Room Temperature and 40 kbar Pressure," J. A. Gladysz and Y. S. Yu, J. Chem. Soc., Chem. Commun., 599 (1978).

"Squeezing the Transition State," J. A. Gladysz, CHEMTECH, **9**, 372 (1979).

"Alkylation and Acylation of the  $[(CO)_4FeSi(CH_3)_3]^-$  Anion; A Novel 1,3-Sigmatropic Shift from Iron to Acyl Oxygen," A. J. Bladeney, W. Krone-Schmidt, and J. A. Gladysz, in preparation for Organometallics.

"Exploratory High Pressure Chemistry," John Gladysz, . Final Technical Report.

### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The initial objective of the research was to study organic and organometallic chemistry at high pressures. However, due to some difficulties encountered in pursuing this line of research (caused in part by the deaths of two key collaborators, Professors William F. Libby and George Kennedy, during the course of this project (they furnished the host laboratory), the scope of the project was expanded to include studies of organosilicon and metal/silicon compounds.

A novel 1,3-sigmatropic shift was observed in the acylation of a silylated iron anion. A high yield cycloaddition of allyl iron complexes to olefins under pressure was carried out. This reaction constitutes a relatively rare example of a 3 plus 2 cycloaddition to give a 5-membered carbocyclic ring. It was found that migratory insertion reactions of transition metal alkyls can be effected by the application of pressure.

AFOSR Program Manager: Dr. Anthony J. Matuszko

## COMPLETED PROJECT SUMMARY

1. TITLE: Synthesis and Characterization of Transition Metal Complex Systems with Novel Solid State Properties
2. PRINCIPAL INVESTIGATOR: Dr. L. V. Interrante  
General Electric Company  
Corporate Research and Development  
Schenectady, NY 12301
3. INCLUSIVE DATES: 1 April 1979 - 31 March 1982
4. CONTRACT NUMBER: F49620-79-C-0051
5. COSTS AND FY SOURCE: \$22,500, FY79; \$45,337, FY80; \$46,576, FY81;  
\$23,739, FY82
6. SENIOR RESEARCH PERSONNEL:

### GE Personnel

Mrs. A. G. Williams  
Dr. J. W. Bray  
Dr. I. S. Jacobs

Dr. H. R. Hart, Jr.  
Dr. J. S. Kasper

### Outside Collaborators

Dr. P. Cassoux, CNRS Laboratory, Toulouse, France  
Dr. J. C. Bonner, University of Rhode Island, Providence, RI  
Dr. D. Moncton, Bell Laboratories  
Drs. D. Bloch and J. Voiron, Laboratoire Louis Neel, CNRS,  
Grenoble, France  
Drs. J. Northby, University of Rhode Island, Providence, RI  
Dr. L. J. de Jongh, Kammerling Onnes Laboratory, Netherlands

### 7. PUBLICATIONS:

"Magnetic Field Effects on TTF  $\text{CuS}_4\text{C}_4(\text{CF}_3)_4$ . A Spin-Peierls System," J. W. Bray, I. S. Jacobs, D. Bloch, D. E. Moncton, D. E. Shirane, J. C. Bonner, and L. V. Interrante, Phys. Rev., **B20**, 2067 (1979).

"Spin-Peierls Phase Diagrams: Observations and Models," I. S. Jacobs, L. V. Interrante, D. Bloch, J. C. Bonner, J. W. Bray, and H. R. Hart, Jr., J. Magnetism and Magnetic Matls., **158**, 332 (1980).

"New High Field Phase in the Spin-Peierls System, (TTF)- $\text{CuS}_4\text{C}_4(\text{CF}_3)_4$ ," D. Bloch, J. Voiron, J. C. Bonner, J. W. Bray, I. S. Jacobs, and L. V. Interrante, Phys. Rev. Letters, **44**, 294 (1980).

"New High-Field Phenomena in Spin-Peierls Systems," I. S. Jacobs, J. W. Bray, L. V. Interrante, D. Bloch, J. Voiron, and J. C. Bonner, Physics in One Dimension, J. Bernasconi and T. Schneider, eds., Springer Series in Solid State Sciences (Springer, Berlin-Heidelberg-New York, 1980) in press.

"New  $\pi$ -Donor Acceptor Compounds Including the First Example in Which Both Donor and Acceptor Are Transition Metal Complexes," P. Cassoux, L. V. Interrante, and J. S. Kasper, C. R. Acad. Sci. Paris, serie C, t. 291, p. 25 (1980).

"Coordination Compounds as a Source of Electrically Conductive Solid State Materials," L. V. Interrante, Coordination Chemistry, 21, Proceedings XXI Intl. Conf. on Coordination Chemistry, Toulouse, France, July 7-11, 1980, J. P. Laurent, ed., Pergamon Press, Oxford (1981), p 87-97.

"Field-Dependent Differential Susceptibility Studies on  $\text{TTF-AuS}_4\text{C}_4(\text{CF}_3)_4$ : Universal Aspects of the Spin-Peierls Phase Diagram," J. A. Northby, H. A. Groenendijk, L. J. deJongh, J. C. Bonner, I. S. Jacobs, and L. V. Interrante, Phys Rev. B., 25, 3215 (1982).

"The Spin-Peierls Transition," J. W. Bray, L. V. Interrante, I. S. Jacobs and J. C. Bonner, GE CRD Report No. 81CRD221, Oct 1981, to be published as a chapter in the series "Extended Linear Chain Compounds," Plenum Publ. Corp., J. S. Miller, ed.

"New  $\pi$ -Donor-Acceptor Compounds Derived from a Macrocyclic Planar Metal Complex," P. Cassoux, L. V. Interrante and J. S. Kasper, Proc. Intn'l. Conference on Low-Dimensional Conductors, Molecular Crystals & Liquid Crystals, in press (1982).

"Synthesis and Characterization of Transition Metal Complex Systems with Novel Solid State Properties," L. V. Interrante, Final Technical Report.

#### 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The primary objectives of this research program were: (1) to elucidate synthetically useful structure-property relationships that ultimately will enable the directed synthesis of transition metal complex systems with desired solid state properties, and (2) to synthesize and characterize new materials with novel solid state electrical and/or magnetic properties.

In pursuit of these objectives, selected for study were particular types of transition metal complexes which have structures and properties appropriate for extended solid state intermolecular interactions and which can be structurally modified so as to permit a systematic investigation of molecular structure-solid state property relationships. The systems chosen include the bis-dithiolene metal complexes, which were used previously by Dr. Interrante and his group as  $\pi$ -acceptors in the preparation of  $\pi$ -donor-acceptor ( $\pi$ -D-A compounds with novel magnetic and electrical properties and various macrocyclic metal complexes which were considered to be promising candidates for use as  $\pi$ -donors in  $\pi$ -D-A compound formation.

The work on the bis-dithiolene metal complexes was focused, in particular, on the further characterization and elaboration of the  $\text{TTF} \cdot \text{MS}_4\text{C}_4(\text{CF}_3)_4$  series of compounds which were found in earlier studies to exhibit novel magnetic properties. Included among these compounds are the first examples of one-dimensional magnetic systems which undergo the spin-Peierls transition, a new magnetoelastic effect first discovered in Interrante's laboratory in 1975 and currently the object of considerable scientific attention worldwide. The studies of the macrocyclic metal complex systems involved the use of both nitrogen and sulfur containing ligands and included efforts to synthesize new macrocyclic systems as well as the preparation, structural characterization, and physical property study of selected  $\pi$ -D-A compounds. In addition, a novel iridium(I) complex was prepared using a new organic ligand system and examined as a source of conductive 1-D materials, employing iodine to partially oxidize the complex units.

The approach to the investigation of these systems involved both the synthesis and characterization of new compounds and the detailed structural and physical study of selected systems in collaboration with scientists at other institutions as well as in the G.E. laboratories. In those cases where evidence for novel solid state properties was obtained, as for example with the  $\text{TTF} \cdot \text{MS}_4\text{C}_4(\text{CF}_3)_4$  compounds, a full range of molecular structural variations was explored, both in order to generate further examples of novel materials and as a means of obtaining information regarding the systems and phenomena in question.

The various compounds were studied using electrical conductivity, magnetic susceptibility, and other solid state property measurement techniques. In addition, their crystal structures were characterized using single crystal x-ray diffraction methods. The results provide new information regarding the solid state interactions in metal complex-containing systems and suggest the promise of such systems as a source of solid state materials with novel magnetic and electronic properties.

AFOSR Program Manager: Dr. Anthony G. Matuszko

# COMPLETED PROJECT SUMMARY

1. TITLE: Synthesis of Novel Fluorine Compounds: New Experimental Challenges in Elemental Fluorine Chemistry
2. PRINCIPAL INVESTIGATOR: Professor Richard J. Lagow  
Department of Chemistry  
The University of Texas at Austin  
Austin, Texas 78712
3. INCLUSIVE DATES: 1 June 1978 - 31 May 1982
4. GRANT NUMBER: AFOSR-78-3658
5. COSTS AND FY SOURCE: \$43,000, FY78; \$45,728, FY79; \$50,000, FY80;  
\$55,000, FY81
6. SENIOR RESEARCH PERSONNEL:

Dr. J. L. Adcock  
Dr. W. I. Bailey, Jr.  
Dr. W. Driehsen

Dr. D. W. Firsich  
Dr. J. A. Morrison

7. JUNIOR RESEARCH PERSONNEL:

R. E. Aikman, Jr.  
T. R. Bierschenk  
G. E. Gerhardt  
M. A. Guerra  
L. A. Harmon  
J. L. Jordan  
T. J. Juhlke

H. N. Huang  
W. H. Lin  
E.K.S. Liu  
R. M. Newman  
S. N. Partovi  
D. F. Persico  
L. J. Turbini

8. PUBLICATIONS:

"Simultaneous Fluorination and Functionalization of Hydrocarbon Polymers," R. J. Lagow, J. L. Adcock and S. Inoue, J. Am. Chem. Soc., 100, 1948 (1978).

"Direct Fluorination of Tetramethyltin. Synthesis of Trifluoromethyltin Compounds," R. J. Lagow and E.K.S. Liu, Inorg. Chem., 17, 618 (1978).

"Trifluoromethylsulfur Trifluoride. An Improved Synthesis, New NMR Data and Stereoschemistry," R. J. Lagow, R. W. Braun, A. H. Cowley and M. C. Cushner, Inorg. Chem., 17, 1679 (1978).

"Synthesis of Perfluoro-Adamantane Compounds by Direct Fluorination," R. J. Lagow, G. Robertson and E.K.S. Liu, J. Org. Chem., 43, 4981 (1978).

"The Synthesis of the Perfluoropoly(ethylene glycol) Ethers by Direct Fluorination," R. J. Lagow and G. E. Gerhardt, J. Org. Chem., 43, 4505 (1978).

"Direct Fluorination: A 'New' Approach to Fluorine Chemistry," R. J. Lagow and J. L. Margrave, Progress in Inorganic Chemistry, 26, 161 (1979).



"The Synthesis of Bis(trifluoromethyl)sulfone and Bis(trifluoromethyl)sulfate by Direct Fluorination," R. J. Lagow and L. A. Harmon, J. Chem. Soc., **8**, 2379 (1979).

"Direct Fluorination of Organic Compounds," R. J. Lagow, R. B. Badachhape, R. H. Hauge and J. L. Margrave, Encyclopedia of Chemical Technology, (1979).

"The Synthesis of Highly Branched Fluorine Compounds; Synthesis and Characterization of F-2, 2, 5, 5-Tetramethylhexane," R. J. Lagow and E.K.S. Liu, J. Fluorine Chem., **13**, 71 (1979).

"New Methods for the Synthesis of Trifluoromethyl Organometallic Compounds," R. J. Lagow and J. A. Morrison, Advances in Inorganic and Radiochemistry, **23**, 199 (1979).

"Evidence for the Synthesis of a 'Stable' Sigma Bonded Xenon-Carbon Compound: Bis(trifluoromethyl)xenon," R. J. Lagow and L. J. Turbini and R. E. Aikman, J. Am. Chem. Soc., **101**, 5833 (1979).

"Synthesis of Highly Branched Perfluoro Ethers by Direct Fluorination, Promising New Materials Based on the Hexafluoroacetone-Ethylene Copolymer," R. J. Lagow, G. E. Gerhardt and E. T. Dumitru, J. Polymer Science, **18**, 157 (1979).

"Scalar Coupling Between Rare Spins in Solids," R. J. Lagow, R. D. Kendrick, C. S. Yannoni and R. E. Aikman, J. Magnetic Resonance, **37**, 555 (1980).

"Synthesis of Perfluoropolyethers by Direct Fluorination; A Novel Preparation for Perfluoro Polymethylene Oxide and Perfluoro Polypropylene Oxide Ethers," R. J. Lagow and G. E. Gerhardt, J. Chem. Soc., Perkin Trans. I, **1321** (1981).

"The Direct Fluorination of Hexamethyldigermane and Hexamethyldisilane," R. J. Lagow and R. E. Aikman, Inorg. Chem., **21**, 524 (1982).

"The Synthesis of Tetrakis(perfluorocyclohexyl)methane and Bis(perfluorocyclohexyl)difluoromethane by Direct Fluorination," R. J. Lagow and R. E. Aikman, J. Org. Chem., **47**, 2789 (1982).

"Synthesis of Functionalized Fluorocarbon Polymers by Direct Fluorination of Pendant Polyesters," R. J. Lagow and R. E. Aikman, J. Am. Chem. Soc., in press.

"The Synthesis of Perfluoropolyethers Via Hydrogen Polyesters: A New General Method," R. J. Lagow, G. E. Gerhardt and D. F. Persico, Polymer Letters, in press.

"The Synthesis of Highly Branched Perfluoro Ethers; A New Fluorocarbon Blood Substitute," R. J. Lagow and D. F. Persico, Tetrahedron Letters, in press.

"Synthesis of the Four Coordinate Perfluorocyclohexyl Compounds of Germanium, Silicon and Tin by Direct Fluorination," R. J. Lagow and D. F. Persico, J. Am. Chem. Soc., in press.

"The Synthesis of  $W(CF_3)_6 \cdot PET_3$  by Direct Fluorination of Hexamethyl Tungsten," R. J. Lagow and R. E. Aikman, J. Am. Chem. Soc., in press.

"Synthesis of Novel Fluorine Compounds: New Experimental Challenges in Elemental Fluorine Chemistry," R. J. Lagow, Final Technical Report.

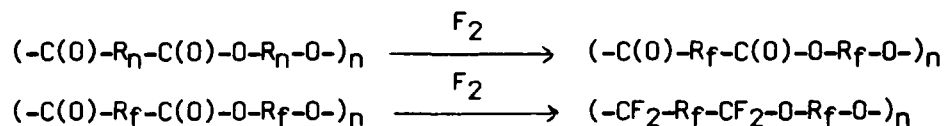
#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The direct fluorination techniques which we have developed in our laboratory at MIT and at the University of Texas over the past several years have developed into a mature and useful synthetic technique. We believe that the synthetic work accomplished recently in our laboratory and in other laboratories in the United States, Europe and Japan has established that direct fluorination is the most generally applicable technique for the synthesis of novel fluorine compounds. That is to say, in cases where there is not an established industrial process for preparation of the new fluorine containing species, direct fluorination has the highest probability of synthetic success.

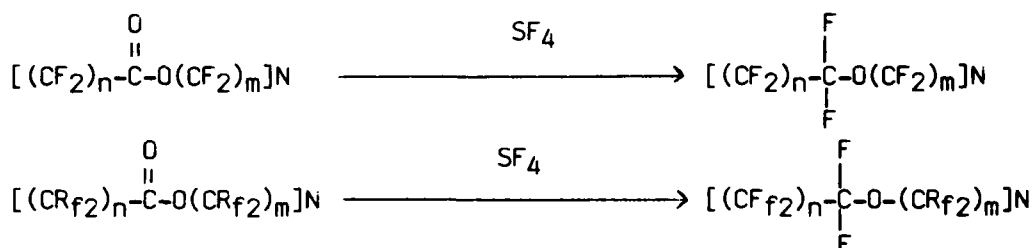
We are in the midst of preparing a series of highly branched ethers and feel that the significance of this series of compounds in terms of new materials applications warrants a very intensive investigation of their synthesis and properties. The highly branched ethers are thermally stable even beyond the more linear perfluoro polypropylene oxide and polyethylene oxide structures which are now marketed by DuPont and Montiedison. Thermal analysis shows that some of the branched polyethers are stable to about 420°C which is considerably more than the 360°-380°C which is standard for polytetrafluoro-ethylene. Further, when these highly branched perfluoropolyethers decompose, they do not carbonize as does polytetrafluoroethylene but rather, depolymerize into shorter chain perfluoropolyether segments. Their specific decomposition products are the subject of current investigation in our laboratory. We have succeeded in making oils, greases, waxes and species of almost any molecular weight desired, including high polymers, from such direct fluorination reactions.

In the synthesis of other structures such as highly branched perfluoro-polyethers, unsymmetrical perfluoropolyethers, and longer carbon chain perfluoropolyethers direct fluorination provides a unique synthetic approach. For example, the polymerization of epoxides produces only a repeating chain of polyethers and if one wants an AB or an ABC polyether structure, the use of a polyester as a starting material is quite an advantage. In fact, there are only about fourteen commercially produced hydrocarbon polyether starting materials. With a new technique to be discussed in the next section, the number of new materials it is possible to produce in the perfluoropolyether area is almost unlimited.

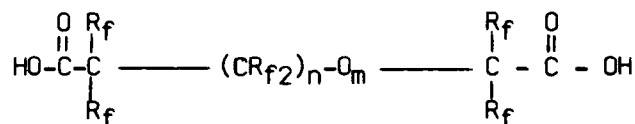
The synthetic scheme which is being used to explore the perfluoropolyethers from hydrocarbon polyesters is:



Perfluoroesters are interesting compounds in their own right, and production by direct fluorination, isolation and characterization of such compounds would be a significant achievement for the technique and the experimentalist. The significance of this work is seen clearly in view of the current absence of any general method for producing perfluoroethers. The resulting perfluoro-polyesters oligomers have been treated with sulfur tetrachloride to convert the carboxylic acid groups to  $CF_2$  groups thus rendering a perfluoro-polyether. We have done this with nonstoichiometric amounts of  $SF_4$  such that there will be left in the structure a number of unreacted ester linkages. The system is then hydrolyzed (perfluoroesters hydrolyze spontaneously) to produce difunctional perfluoropolyesters with the following structures:



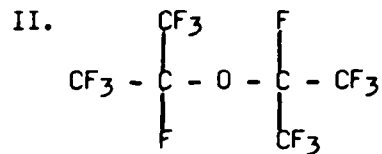
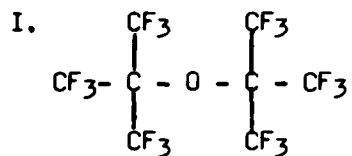
Thus hydrolysis of the remaining ester groups will lead to the isolation of perfluorocarbon ether diacids:



Recently in our laboratory, we have prepared two very interesting carbon-substituted methanes, tetrakis(perfluorocyclohexyl)methane and bis(perfluorocyclohexyl)methane. These compounds were prepared because they are thought to have very advantageous steric properties for use as fluorocarbon oxygen carriers, as blood substitutes, and for other applications. The tetrakis compound is a very stable glass-like material and its appearance and stereochemistry make it interesting structurally. A single crystal X-ray study is underway.

It has occurred to us that this same general procedure should be useful for synthesis of perfluorocyclohexyl organometallic compounds most of which are not known. We have preliminary results on the reaction of fluorine with tetraphenylgermane, tetraphenylsilane, tetraphenyltin and tetraphenyllead. We are also interested in the study of perfluorocyclohexyl group III and group V elements.

We have also prepared recently, by direct fluorination, and currently have under study, the perfluorocarbon polyethers:



These materials were previously unknown. Because they have steric bulk, they are thought to be of interest as oxygen carriers in the artificial blood substitute area.

AFOSR Program Manager: Dr. Anthony J. Matuszko

## COMPLETED PROJECT SUMMARY

1. TITLE: Fabricable Polymers for Matrices and Adhesives Which Are Extremely Stable to Heat, Oxidation, and Hydrolysis
2. PRINCIPAL INVESTIGATOR: Professor Carl S. Marvel  
Department of Chemistry  
University of Arizona  
Tucson, AZ 85721
3. INCLUSIVE DATES: 1 October 1976 - 31 December 1981
4. GRANT NUMBER: AFOSR-77-3112
5. COSTS AND FY SOURCE: \$96,097, FY77; \$51,589, FY78; \$45,955, FY80  
\$49,572, FY81
6. SENIOR RESEARCH PERSONNEL:

Dr. Richard L. Frentzel  
Dr. Robert S. Cutler  
Dr. Steve K. Huang  
Dr. Steven R. Morehead  
Dr. Shiow-Ching Lin  
Dr. Venkatesa Sankaran

Dr. Andreas Somers  
Dr. Paul Chen  
Dr. George Kriek  
Dr. See Lin  
Dr. B. H. Lee

### 7. PUBLICATIONS:

"New Processable Polyaromatic Ether-Keto-Sulfones Curable by Intramolecular Cyclization," Shiow-Ching Lin and C. S. Marvel, J. Polym. Sci., Polym. Chem. Ed., 17, 2337-2350 (1979).

"Polyaromatic Ether-Ketone-Sulfones Containing 1,3-Butadiene Units," V. Sankaran and C. S. Marvel, J. Polym. Sci., Polym. Chem. Ed., 17, 3949-3957 (1979).

"Heat-Curable Polyaromatic Keto-Ether-Sulfones. XIV. More Polymers with 2,2'-Diphenylethynyl-4,4'-Diphenyl Units and Their Rearrangement Products," Richard L. Frentzel and C. S. Marvel, J. Polym. Sci., Polym. Chem. Ed., 17, 1073-1087 (1979).

"New Processable Polyaromatic Amides Curable by Intramolecular Cyclization. XVI," V. Sankaran, Shiow-Ching Lin and C. S. Marvel, J. Polym. Sci., Polym. Chem. Ed., 18, 495-503 (1980).

"New Processable Poly(ether-Keto-Sulfone)s, Poly(arylene Sulfone)s, and Polyesters Curable by Intramolecular Cyclization. XVII," A. Somers and C. S. Marvel, J. Polym. Sci., Polym. Chem. Ed., 18, 1511-1521 (1980).

"New Processable Polyaromatic Ether-Keto-Sulfones Curable by Diels-Alder Cycloaddition," V. Sankaran and C. S. Marvel, J. Polym. Sci., Polym. Chem. Ed., 18, 1821-1834 (1980).

"New Processable Polyaromatic Esters Curable by Intramolecular Cyclization. XVIII," Paul Y. Chen and C. S. Marvel, J. Polym. Sci., Polym. Chem. Ed., 19, 619-627 (1981).

"New Processable Polyaromatic Ether-Keto-Sulfones as Colorless, Clear Film-Forming Materials," Byung H. Lee and C. S. Marvel, in press.

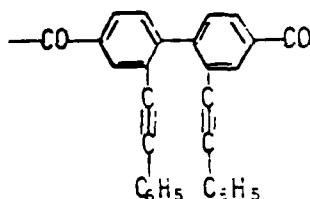
"New Processable Polyaromatic Keto-Sulfones with Internal Acetylene Units," See Lin, George R. Kriek and C. S. Marvel, in press.

"Fabricable Polymers for Matrices and Adhesives Which Are Extremely Stable to Heat, Oxidation, and Hydrolysis," Carl S. Marvel, Final Technical Report.

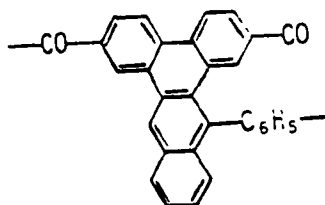
#### 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The object of this research was to prepare fabricable new exceptionally stable polymers containing groups which formed new intermolecular rings and thus raised the softening point of the resins when in place so they could withstand temperatures up to 700°F. These resins then could be used as laminates and adhesives in aircraft.

Dr. Frentzel and Dr. Cutler worked on polyaromatic ketones containing the unit



which could be cured by heating to give the unit



These polymers produced good laminates but were somewhat intractable and did not have as good oxidation stability as hoped for.

Dr. Shiow-Ching Lin developed a satisfactory synthesis of 2,2'-dibromo-4,4'-diphenic acid which he converted by Friedel-Craft reaction with 4,4'-diphenoxydiphenyl sulfone and isophthaloyl chloride, and he later treated that polymer with copper phenylacetylene to obtain the 2,2'-diphenylethynyl derivative, which gave an interesting laminating resin.

Dr. Sankaran prepared the p,p'-dicarboxylic acid of 1,4-diphenyl-1,3-butadiene, and by Friedel-Craft reaction with diphenyl ether, obtained the polymer which was very difficult to fabricate, and hence not tested further.

Dr. Somers made polyether-ketone-sulfones, polyarylene sulfones, and polyesters which were curable by molecular cyclization. The products were expensive and were not developed further.

Dr. Sankaran and Dr. Shiow-Ching Lin prepared a variety of poly-aromatic amides which could be cured by intramolecular cyclization, and these gave promising laminating resins.

Dr. Chen prepared a series of polyaromatic esters which could be cured by the intramolecular cyclization method. These esters were easily soluble and tractable before curing. After curing they were insoluble with increased thermo-stability. The curing process raised the softening temperature by about 20°C and increased the heat stability of the polymers. They lost very little weight at 300°C in circulating air for three days. They made good laminates. The curing requires 270° for 30 hours, which is a drawback to their practical use.

Dr. See Lin and Dr. Lee worked on the m- and p-dicarboxylic acid derivatives of diphenylacetylene and prepared very interesting polymers by Friedel-Craft reaction with diphenyl ether and diphenoxydiphenyl sulfone. Both the meta and the para isomers gave excellent, clear films which remain clear up to nearly 300°C, and seem to offer promise as replacements for polymethyl methacrylate as a canopy for fighter planes. Although it was possible to get perfectly clear, thin films, it was not possible to melt the product to obtain large pieces such as would be needed for canopies without a yellowing developing, which made them seem less promising than before. They still are under consideration but do not seem as promising as they first did.

At the present time, Dr. See Lin is working on a p-cyclophane derivative in which the bridged portion between the two rings is fluorinated, and then this is converted to the keto ether with isophthaloyl chloride. The product is quite stable to heating and oxidation and can be cured on heating. It does give a laminate but this is still under study and not ready for final evaluation.

Dr. Lee is currently working with 1,5-diamino-2,6-dimercaptoanthraquinone and condensing it with a 2,5-dichlorobenzoquinone to obtain a new type of polymer which is very heat stable but also very intractable. We are still studying it to find a way to convert it into a useful polymer.

AFOSR Program Manager: Dr. Anthony J. Matuszko



# COMPLETED PROJECT SUMMARY

1. TITLE: Synthesis of Phosphotriazines for Potential High Temperature Fluids and Elastomers Application
2. PRINCIPAL INVESTIGATOR: Dr. K. L. Paciorek  
Ultrasystems, Inc.  
2400 Michelson Drive  
Irvine, CA 92715
3. INCLUSIVE DATES: 1 March 1979 - 28 February 1982
4. CONTRACT NUMBER: F49620-79-C-0037
5. COSTS AND FY SOURCE: \$29,167, FY79; \$50,000, FY80; \$50,000, FY81;  
\$29,167, FY82
6. SENIOR RESEARCH PERSONNEL:

Dr. T. I. Ito  
Dr. J. H. Nakahara

Dr. D. H. Harris  
Dr. R. H. Kratzer

## 7. PUBLICATIONS:

"Symmetrical Diphosphatetraazacyclooctatetraenes," K. L. Paciorek, R. H. Kratzer, T. I. Ito, and J. H. Nakahara, U.S. Patent 4, 281, 185, issued July 28, 1981.

"Unsymmetrical Diphosphatetraazacyclooctatetraenes," K. L. Paciorek, R. H. Kratzer, T. I. Ito, and J. H. Nakahara, U.S. Patent 4, 297, 510, issued October 27, 1981.

"Diphosphatetraazacyclooctatetraenes. II. Properties and Degradations," K. L. Paciorek, T. I. Ito, J. H. Nakahara, and R. H. Kratzer, J. Fluorine Chem., 16, 441 (1980).

"Diphosphatetraazacyclooctatetraenes. III. Polymerization Studies," K. L. Paciorek, R. H. Kratzer, T. I. Ito, and J. H. Nakahara, to be submitted to the Journal of Fluorine Chemistry.

"Phospha-s-triazines. VI. Polymeric Systems," K. L. Paciorek, R. H. Kratzer, T. I. Ito, and J. H. Nakahara, to be submitted to the Journal of Fluorine Chemistry.

"Phospha-s-triazines. VII. Phenyl-Bridged Phospha-s-triazines," K. L. Paciorek, R. H. Kratzer, T. I. Ito, and J. H. Nakahara, to be submitted to the Journal of Fluorine Chemistry.

"Phenyl-Bridged Phospha-s-triazines," K. L. Paciorek, R. H. Kratzer, T. I. Ito, and J. H. Nakahara, Patent Disclosure, in preparation.

"Synthesis of Phosphatriazines for Potential High Temperature Fluids and Elastomers Application," K. L. Paciorek, R. H. Kratzer, T. I. Ito, and J. H. Nakahara, Final Technical Report.

#### 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of the research was to prepare and characterize monomeric and mono- and diphospha-s-triazine ring compounds with fluorocarbon and fluorocarbon ether side groups as potential high temperature fluid additives and elastomers materials.

The symmetrical and unsymmetrical tetraazacyclooctatetraenes synthesized were found to be thermally less stable than the analogously substituted six-membered phospho-s-triazines. Both materials at 316°C underwent transformation to phospho-s-triazines; the symmetrical arrangement giving diphospha-s-triazine and the corresponding nitrile; the unsymmetrical isomer forming monophospha-s-triazine and diphenylphosphazene trimer. No polymeric compounds could be synthesized having the symmetrical octatetraene ring arrangement as a chain component; only bicyclics were formed. Unsymmetrical polydiphosphatetraazacyclooctatetraenes having thermal and thermal oxidative stabilities directly comparable to those of their monomeric analogues were successfully prepared.

Two polymeric systems involving phospho-s-triazine units were synthesized: poly(monophospha-s-triazines) and monocyclic mono- and diphospha-s-triazines substituted by polyperfluoroalkylether chains on the ring carbon atoms. The latter materials had molecular weights of ~ 5000 and exhibited good thermal and oxidative stability. The molecular weight of poly(monophospha-s-triazines) was ~ 7000; these materials were found to undergo some degradation at 235°C in air.

A novel bis(trichlorophosphorane) intermediate, necessary for the preparation of aryl-linked dumbbell- and poly-(monophospha-s-triazines), was synthesized by a 4-step process in an overall 58% yield. The interaction of the bis(trichlorophosphorane) with perfluoroalkyl- and perfluoroalkyl-etherimidolyamides afforded the desired phenyl-bridged dumbbell monophospha-s-triazines. Electron impact fragmentation patterns of these compounds could be correlated with those of the monomeric monophospha-s-triazines. The thermal and thermal oxidative stability of the phenyl-bridged materials was lower than that of the corresponding monomeric mono- and diphospha-s-triazines.

All the six- and eight-membered heterocyclics synthesized under this program were found to possess antioxidative and anticorrosive properties when utilized as additives for poly(hexafluoropropene oxide) fluids in the presence of M-50 alloy. The polyperfluoroalkylether-substituted phospho-s-triazines were the most effective of the compositions tested. A monophospha-s-triazine was the only member of the series evaluated as an additive in Fomblin Z and E-fluids, where it exhibited better action than that shown by other types of additives.

AFOSR Program Manager: Dr. Anthony J. Matuszko

# COMPLETED PROJECT SUMMARY

1. TITLE: A Study of the Interaction of Hydrazine, Methylhydrazine, and Unsym-dimethylhydrazine with Porphyrins, Metallophorphyrins and Some Metal Coordination Compounds
2. PRINICPAL INVESTIGATOR: Dr. Albert N. Thompson, Jr.  
Department of Chemistry  
Spelman College  
Atlanta, GA 30314
3. INCLUSIVE DATES: 1 June 1982 - 31 August 1982
4. GRANT NUMBER: AFOSR-82-0137
5. COSTS AND FY SOURCE: \$9,982, FY82 (Mini Grant)
6. JUNIOR RESEARCH PERSONNEL: Sonya Maxwell
7. PUBLICATIONS:

"A Study of the Interaction of Hydrazine, Methylhydrazine, and Unsym-dimethylhydrazine with Porphyrins, Metallophorphyrins and Some Metal Coordination Compounds," Albert N. Thompson, Jr., Final Technical Report.

## 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Trisodium pentacyanoferrate (TPF) forms derivatives with hydrazine, methylhydrazine, and unsym-dimethylhydrazine. Each of these derivatives are similar in color and each of the derivatives have similar visible spectra. Separation of these derivatives by HPLC could offer a rapid analytical method of determining the composition of mixtures of the hydrazines.

The photoreduction of Zn-tetraphenylporphyrin (Zn-TPP) with hydrazine, methylhydrazine, and unsym-dimethylhydrazine in phridine was investigated. Results indicate that the presence of hydrazine in mixture with methylhydrazine, and unsym-dimethylhydrazine can be confirmed due to the formation of a unique color that is not produced when Zn-TPP is photo-reduced with methylhydrazine, and unsym-dimethylhydrazine.

Organometallic compounds more sensitive to reduction by hydrazine and porphyrin derivatives that may possibly form hydrazone derivatives with hydrazine are currently being investigated.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Organosilicon Compounds and Organosilicon Polymer Intermediates
2. PRINCIPAL INVESTIGATOR: Dr. Dietmar Seyferth  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139
3. INCLUSIVE DATES: 1 October 1978 - 30 September 1982
4. GRANT NUMBER: AFOSR-79-0007
5. COSTS AND FY SOURCE: \$45,000, FY79; \$46,472, FY80; \$65,000, FY81;  
\$66,381, FY82
6. SENIOR RESEARCH PERSONNEL:  

Dr. C. Prud'homme	Dr. J. Escudie
Dr. J. Pornet	Dr. W.-L. Wang
7. JUNIOR RESEARCH PERSONNEL:  

M. L. Shannon	E. W. Goldman
H. P. Withers, Jr.	R. M. Simon
R. M. Weinstein	T. G. Wood
8. PUBLICATIONS:  

"Reactions of Siliranes with Elemental Sulfur and with t-Butyl Mercaptan. Preparation of the 2,3-Dithia-1-Silacyclopentane Ring System," D. Seyferth, D. P. Duncan and C. K. Haas, J. Organometal. Chem., **164**, 305 (1979).

"Unusual Lithium Transfer Reactions in Lithium-Substituted Organosilicon Compounds. Reinvestigation of the Reaction of 1,8-Dilithionaphthalene with Trimethylchlorosilane," R. J. Wroczynski, M. W. Baum, D. Kost, K. Mislow, S. C. Vick, and D. Seyferth, J. Organometal. Chem., **170**, C29 (1979).

"[1]Ferrocenophanes with Phosphorus and Arsenic as the Bridging Atoms: Synthesis and Some Reactions. A New Route to Ferrocenyllithium Reagents," D. Seyferth and H. P. Withers, Jr., J. Organometal. Chem., **185**, C1 (1980).

"The Elusive Germa- and Stanna-cyclopropanes. Attempted Preparation by the Reaction of 1,3-Dihalides with Magnesium," D. Seyferth, M. Massol, J. Barrau and S. Monteverdi, J. Organometal. Chem., **185**, 307 (1980).

"The Reaction of the Trimethylchlorosilane/Magnesium Reagent with gem-Dibromocyclopropanes," D. Seyferth and D. P. Duncan, J. Organometal. Chem., **187**, 1 (1980).

"A Gas Kinetic Study of the Pyrolysis of Octamethyl-1,2-disilacyclobutane," I.M.T. Davidson, N. A. Ostah, D. Seyferth, and D. P. Duncan, J. Organometal. Chem., **187**, 297 (1980).

"Tetramethylcyclopropyllithium: Stability in Diethyl Ether and Reactions with Trimethylchlorosilane and Trimethyltin Chloride," D. Seyferth and D. D. Dagani, Synth. React. Inorg. Metal-Org. Chem., **10**, 137 (1980).

"2,4-Pentadienyltrimethylsilane: A Useful Pentadienylation Reagent," D. Seyferth and J. Pornet, J. Org. Chem., **45**, 1721 (1980).

"Hexamethylsilirane: Ring Cleavage by Germanium and Tin Hydrides," D. Seyferth, J. Escudie, M. L. Shannon and J. Satge, J. Organometal. Chem., **198**, C51 (1980).

"Hexamethylsilirane. I. Preparation, Characterization and Thermal Decomposition," D. Seyferth, D. C. Annarella, S. C. Vick, and D. P. Duncan, J. Organometal. Chem., **201**, 179 (1980).

" $\eta^5$ -Pentadienyltricarbonylmanganese, an "Open" Analog of Cymantrene," D. Seyferth, E. W. Goldman, and J. Pornet, J. Organometal. Chem., **208**, 189 (1981).

"Hexamethylsilirane. II. Ring-Opening Reactions with Some Simple Reagents," D. Seyferth, D. C. Annarelli, M. L. Shannon, J. Escudie, and D. P. Duncan, J. Organometal. Chem., **225**, 177 (1982).

"Bis(iodomethyl)mercury as a  $\text{CH}_2$  Transfer Reagent," D. Seyferth, C. K. Haas and D. Dagani, J. Indian Chem. Soc., **59**, 111 (1982).

"Phosphorus- and Arsenic-Bridged [1]Ferrocenophanes. I. Synthesis and Characterization," D. Seyferth and H. P. Withers, Jr., Organometallics, **1**, 1275 (1982).

"Phosphorus- and Arsenic-Bridged [1]Ferrocenophanes. II. Synthesis of Poly(1,1'-ferrocenylenephosphine): Oligomers and Polymers," H. P. Withers, Jr., D. Seyferth, J. D. Fellman, P. E. Garrou and S. Martin, Organometallics, **1**, 1283 (1982).

"Hexamethylsilirane. III. Dimethylsilylene Transfer Chemistry," D. Seyferth, D. C. Annarelli and D. P. Duncan, Organometallics, **1**, 1288 (1982).

"High-Yield Acyl Anion Trapping Reactions: A Synthesis of Acyltrimethylsilanes," D. Seyferth and R. M. Weinstein, J. Am. Chem. Soc., **104**, 5534 (1982).

"A Useful Dienemethylation Reagent: (2,4-Pentadienyl)trimethylsilane," D. Seyferth, J. Pornet and R. M. Weinstein, Organometallics, **1**, 1651 (1982).

"Organosilicon Compounds and Organosilicon Polymer Intermediates," D. Seyferth, Final Scientific Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to study the synthesis and properties of new organosilicon compounds. The accomplishments include the following:

a. Studies of the highly reactive Si-C bonds of hexamethylsilacyclopropane and 1,1-dimethyl-3,4-bis(trimethylsilyl)-1-silacyclopropene and of the reactive Si-Si bond of octamethyl-1,2-disilacyclobutane were completed.

b. RP- and RAs- bridged (1)ferrocenophanes were prepared and their reactions with organolithium reagents studied. Ferrocenylenephosphine polymers were prepared for use as ligands in catalysis studies. Their cobalt complexes are active hydroformylation catalysts.

c.  $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CHCH}=\text{CH}_2$  was prepared and found to be a very useful  $\text{CH}_2\text{CH}=\text{CHCH}=\text{CH}_2$  transfer agent to organic carbonyl compounds via an  $\text{SE}_2'$  mechanism.

d. A novel and useful route to acylsilanes based on the carbon monoxide-derived acyllithium reagents has been developed.

e. The hydrolysis of dichlorosilane,  $\text{H}_2\text{SiCl}_2$ , was found to give cyclic oligomers,  $(\text{H}_2\text{SiO})_n$ , with  $n = 4$  through 23, in decreasing amounts. Linear species,  $\text{Me}_2\text{RSiO}(\text{H}_2\text{SiO})_n\text{-SiMe}_2\text{R}$  ( $\text{R} = \text{H}, \text{Me}$ ), also were prepared and studied.

f. A study of the transition metal chemistry of cyclo- $(\text{iPr}_2\text{Si})_4$  was initiated with the ultimate objective of preparing transition metal silicides.

g. A study of the reactivity of  $\text{CaSi}_2$ - derived "reactive silicon" and "silicon mono halides" was started.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Chemical Reactions and Properties of Organosilicon Compounds Related to New Materials

2. PRINCIPAL INVESTIGATOR: Professor Robert West  
Department of Chemistry  
University of Wisconsin  
Madison, WI 53706

3. INCLUSIVE DATES: 1 February 1978 - 31 January 1982

4. GRANT NUMBER: AFOSR-78-3570

5. COSTS AND FY SOURCE: \$68,729, FY78; \$72,530, FY79; \$80,482, FY80;  
\$87,391, FY81

6. SENIOR RESEARCH PERSONNEL:

Dr. Koichi Matsumura

7. JUNIOR RESEARCH PERSONNEL:

David Stanislawski  
A. C. Buchanan III  
Lawrence Brough  
Timothy Drahnak  
Thomas Newman  
Lawrence D. David  
Bradley Helmer  
Corey Carlson

Cynthia Wadsworth  
Mark Fink  
Mike Michalczyk  
Fathieh Shafiee  
Dennis Bean  
Douglas DeYoung  
Jonathan Rich

8. PUBLICATIONS:

"Medium-Ring Cyclosilanes from the Reaction of Dimethyldichlorosilane with Lithium," K. Matsumura, L. F. Brough and R. West, J. C. S. Chem. Commun., 1092 (1978).

"Pulsed  $^1\text{H}$  NMR Studies of Molecular Motion and Plastic Crystallinity in Dodecamethylcyclohexasilane," D. W. Larsen, B. A. Soltz, F. E. Sary and R. West, J. C. S. Chem. Commun., 1093 (1978).

"ESR Studies of Aryl-Substituted Cyclopolysilane Anion-Radicals," A. C. Buchanan III and R. West, J. Organometal. Chem., 172, 273 (1979).

"Dimethylsilylene,  $(\text{CH}_3)_2\text{Si}$ ," T. J. Drahnak, J. Michl and R. West, J. Am. Chem. Soc., 101, 5427 (1979).

"The Crystal and Molecular Structure of the Molybdenum Tetracarbonyl Complex of 1,4-Diphenyl-2,2', 3,3', 5,5', 6,6'-octamethylcyclo-1, 4-diphospha-2,3,5,6-tetrahexane," J. C. Calabrese, R. T. Oakley, and R. West, Can. J. Chem., 57, 1909 (1979).

"Basicity of Siloxanes, Alkoxysilanes and Ethers toward Hydrogen Bonding," R. West, L. S. Wilson, and D. L. Powell, J. Organometal. Chem., 178, 5 (1979).

"Novel Organosilicon Radical Cations," H. Bock, W. Kaim, M. Kira, and R. West, J. Am. Chem. Soc., 101, 7667 (1979).

"The Homologous Series of Cyclic Polysilanes," L. Brough, K. Matsumura and R. West, Angew. Chem. Intl. Ed. Engl., 18, 955 (1979).

"Organosilicon Chemistry," R. West and T. J. Barton, J. Chem. Ed., 57, 165 (1980) Part I; 57, 334 (1980) Part II.

"Molecular Motion in Brittle and Plastic Dodecamethylcyclohexasilane and Decamethylcyclopentasilane," D. W. Larsen, B. A. Soltz, F. Stary, and R. West, J. Phys. Chem., 84, 1340 (1980).

"Cyclic Polysilanes. XIX. A Temperature Study of Redistribution Equilibria between Permethylcyclopolysilanes," L. F. Brough and R. West, J. Organometal. Chem., 194, 139 (1980).

"Perethylcyclopolysilanes:  $(Et_2Si)_4$  through  $(Et_2Si)_8$ ," C. W. Carlson, K. Matsumura, and R. West, J. Organometal. Chem., 194, C5 (1980).

"Synthesis and Spectral Properties of Group V Heteroatompermethylcyclopolysilanes,  $MeN(SiMe_2)_n$  and  $MeP(SiMe_2)_n$ ," T. H. Newman, R. West, and R. T. Oakley, J. Organometal. Chem., 197, 159 (1980).

"Synthesis and Crystal Structures of Two Iron Derivatives of Permethylcyclopentasilane," T. J. Drahnak, R. West, and J. C. Calabrese, J. Organometal. Chem., 198, 55 (1980).

"Sulfur and Selenium Insertion into the Silicon-Silicon Bond in Decamethylcyclopentasilane," M. Wojnowska, W. Wojnowski, and R. West, J. Organometal. Chem., 199, C1 (1980).

"Organosilyl Substituted Phosphoranyl Radicals," T. H. Newman and R. West, J. Organometal. Chem., 199, C39 (1980).

" $^{29}Si$  and  $^{13}C$  Spectra of Permethylpolysilanes," D. A. Stanislawski and R. West, J. Organometal. Chem., 204, 295 (1981).

" $^{29}Si$  and  $^{13}C$  NMR Spectra of Chloro- and Fluorosubstituted Linear Permethylpolysilanes," D. A. Stanislawski and R. West, J. Organometal. Chem., 204, 307 (1981).

"Photoisomerization of Dimethylsilylene to 2-Silapropene and Thermal Reversion to Dimethylsilylene," T. J. Drahnak, J. Michl, and R. West, J. Am. Chem. Soc., 103, 1845 (1981).

"Reversible Di- $\pi$ -Methane Rearrangements of Bicyclic Organosilicon Compounds," J. D. Rich, T. J. Drahnak, R. West, and J. Michl, J. Organometal. Chem., 212, C1 (1981).



"The Permethylcyclosilanes  $(\text{Me}_2\text{Si})_5$  through  $(\text{Me}_2\text{Si})_{35}$ ," L. F. Brough and R. West, J. Am. Chem. Soc., **103**, 3049-3056 (1981).

"Phenylmethylpolysilanes: Formable Silane Copolymers with Potential Semiconducting Properties," R. West, L. D. David, P. I. Djurovich, K. L. Stearley, K. S. V. Stinivasan, and H. Yu, J. Am. Chem. Soc., **103**, 7352-7354 (1981).

"Tetramesityldisilene, A Stable Compound Containing a Silicon-Silicon Double Bond," R. West, M. J. Fink, and J. Michl, Science, **214**, 1343 (1981).

"Synthesis and Dynamic NMR Studies of the Heterocyclic Diphosphacyclopoly-silanes,  $(\text{PhP})_2(\text{SiMe}_2)_n$ . Crystal and Molecular Structure of  $(\text{PhP})_2(\text{SiMe}_2)_3$ ," T. H. Newman, J. C. Calabrese, R. T. Oakley, D. A. Stanislawski, and R. West, J. Organometal. Chem., **225**, 211-224 (1982).

#### Submitted

"Organic Chemistry Based on Silicon: The Cyclic Permethylpolysilanes," R. West, China-Japan-U.S. Symposium Proceedings, June 1981.

"Organopolysilanes," R. West in Comprehensive Organometallic Chem., E. Abel (ed), Pergamon Press Ltd., Oxford, England, 1981, Ch. 9.4.

"Electron-Donation of Methylpolysilanyl Groups:  $\sigma$  + Constants from  $^{13}\text{C}$  NMR Spectroscopy," L. F. Brough and R. West, J. Organometal. Chem.

"Electron Delocalization and 'Aromatic' Behavior in Cyclic Polysilanes," R. West, Pure Appl. Chem.

"Polysilastylene: Phenylmethylsilane-Dimethylsilane Copolymers as Precursors to Silicon Carbide," R. West, L. D. David, P. I. Djurovich, H. Yu, and R. Sinclair, J. Am. Ceram. Soc.

"Formation of Cyclic Silicon-Silicon Systems," R. West in "Inorganic Reactions and Methods," J. J. Zuckerman, ed., Verlag Chemie.

"Chemical Reactions and Properties of Organosilicon Compounds Related to New Materials," Robert West, Final Technical Report.

#### 9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research involved the synthesis of new organosilicon compounds and polysilane polymers, together with studies of their chemical and physical properties. The following is a summary of the accomplishments:

A. Polysilane copolymers containing phenylmethylsilyl and dimethylsilyl units have been prepared and characterized. These soluble polymers ("polysilastyrene") can be melted, molded, cast into films or drawn into fibers; when exposed to ultraviolet light they undergo

crosslinking, becoming rigid and insoluble. Heating above 800°C converts the polymers to silicon carbide. Polysilastyrene and related polymers may have applications in semiconductor and ceramics technology.

B. Divalent silicon compounds (silylenes) have been made by photolysis and studied in hydrocarbon or argon matrices.

C. The first compound containing a silicon-silicon double bond has been synthesized and partially characterized. The compound is tetramesityldisilene,  $(\text{Mes})_2\text{Si}=\text{Si}(\text{Mes})_2$  ( $\text{Mes} = 2,4,6\text{-trimethylphenyl}$ ), made by photolysis of  $(\text{Me}_3\text{Si})_2\text{Si}(\text{Mes})_2$ .

D. Numerous other advances in the chemistry of alkylpolysilanes have been accomplished, including synthesis of the entire series of cyclic methylsilanes  $(\text{Me}_2\text{Si})_n$ ,  $n = 5$  to 35; studies of the interconversion and the thermodynamic stability of  $(\text{Me}_2\text{Si})_n$  oligomers; synthesis of cyclic ethylsilanes,  $(\text{Et}_2\text{Si})_n$ , of organosilicon rotanes,  $[(\text{CH}_2)_4\text{Si}]_n$ , and of phospho- and aza-cyclosilanes; and study of electronic behavior of cyclosilanes using electron spin resonance, uv and NMR spectroscopy.

AFOSR Program Manager: Dr. Anthony J. Matuszko

RESEARCH EFFORTS COMPLETED IN FY82

ATMOSPHERIC SCIENCES - LT COL TED S. CRESS

Modeling the Ionospheric and  
Plasmaspheric Effects Created by  
the HEAO-C Launch  
AFOSR-ISSA-78-0016; -79-0005,  
AFOSR-ISSA-80-0016; -81-0020

David N. Anderson  
Space Environment Laboratory  
NOAA Environmental Research  
Laboratories  
Boulder CO 80303

Remote Lidar Measurement of Wind,  
Turbulence, and Convective  
Structure in the Planetary  
Boundary Layer  
AFOSR-MIPR-80-00041

Edwin Eloranta  
Department of Meteorology  
University of Wisconsin  
Madison, WI 53706

Studies of the Morphology of the  
High Latitude Ionosphere  
F19628-80-C-0002

J. V. Evans  
Haystack Observatory  
Massachusetts Institute  
of Technology  
Westford, MA 01886

Shear Excitation of Atmospheric  
Gravity Waves  
F49620-81-C-0009

David C. Fritts  
Physical Dynamics, Inc.  
P.O. Box 3027  
Bellevue, WA 98009

Global Atmospheric Waves;  
Mechanical Heating of the  
Lower Thermosphere  
AFOSR-82-0052

G. V. Groves  
Department of Physics and  
Astronomy  
University College London  
Gower Street  
London, WC1E 6BT, England

Analysis of NOAA Alaskan MST Radar  
System Data  
AFOSR-80-0020

Michael C. Kelley  
School of Electrical Engineering  
Cornell University  
Ithaca, NY 14853

Investigation of Shear-Induced  
Turbulence by MST Radar  
AFOSR-80-0286

Gerald J. Romick  
Kolf Jayaweera  
Geophysical Institute  
University of Alaska  
Fairbanks, Alaska 99701

Project Definition Study for  
National STORM Program  
AFOSR-ISSA-81-00040

Stanley Ruttenberg  
Office of Scientific Program  
Development  
University Corporation for  
Atmospheric Research  
Boulder, CO 80307

## COMPLETED PROJECT SUMMARY

1. TITLE: (1) Modeling the Effects of an H<sub>2</sub> Gas Release on the Equatorial Ionosphere  
(2) Modeling the Ionospheric Effects of Two Chemical Releases over Hawaii  
(3) Modeling the Ionospheric and Plasmaspheric Effects Produced by a Simulated Saturn V Launch  
(4) Modeling the Ionospheric and Plasmaspheric Effects Created by the HEAO-C Launch
2. PRINCIPAL INVESTIGATOR: Dr. David N. Anderson  
Space Environment Laboratory  
NOAA Environmental Research Laboratories  
Boulder CO 80303
3. INCLUSIVE DATES: 1 January 1978 - 30 September 1981
4. GRANT NUMBERS: AFOSR-ISSA-78-0016, AFOSR-ISSA-79-0005,  
AFOSR-ISSA-80-0016, AFOSR-ISSA-81-0020
5. COSTS AND FY SOURCE: \$7,000, FY78; \$7,000, FY79; \$14,000, FY80;  
\$14,000, FY81
6. SENIOR RESEARCH PERSONNEL: Dr. Arjun Tar. (FY80)
7. JUNIOR RESEARCH PERSONNEL: Bruce Herniter (FY81)
8. PUBLICATIONS:  
  
"The Motion of Depleted Plasma Regions in the Equatorial Ionosphere,"  
D. N. Anderson and G. Haerendel, J. Geo. Res., 84, 4251 (1979)  
  
"Composition of the Nighttime Ionospheric F1 Region Near the Magnetic  
Equator," D. N. Anderson and D. N. Rusch, J. Geo. Res., 85, 569 (1980)  
  
"Modeling the Ambient, Low Latitude F-Region Ionosphere - A Review,"  
D. N. Anderson, J. Atmos. Terr. Phys., 43, 753 (1981)  
  
"Neutral Wind Effects on the Equatorial F-Region Ionosphere," D. N.  
Anderson and R. G. Roble, J. Atmos. Terr. Phys., 43, 835 (1981)
9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This series of research projects aimed at the improved understanding of several aspects of ionospheric modification by chemical releases. During the first year, a model of chemical reactions in the ionosphere was used to study plasma depletions resulting from releases of hydrogen, either at

a point or along a magnetic field line, and to determine the subsequent motion of the depleted region. The second year's effort examined the effects of releases of  $H_2O$ ,  $CO_2$ , and  $N_2$  for comparison with remote and in situ observations of ion and electron densities following two 1977 chemical releases. Subsequent work applied the model to the effects of space operations, specifically, the simulated launch of a Saturn V and the actual launch of the third High Energy Astrophysical Observatory (HEAO-C) on an Atlas/Centaur in 1979.

The vertical  $\bar{E} \times \bar{B}$  motion of depleted plasma regions in the equatorial ionosphere was investigated by incorporating flux-tube integrated quantities of electron content and Pedersen conductivity. A simple expression for the polarization electric field,  $\bar{E}_1$ , inside the depleted flux tube, was used. The resulting calculations revealed that the vertical bubble velocity as a function of time critically depended on the background ionospheric electric field and that this dependence extended to much greater heights than previously thought. Bubbles initiated at 350 km altitude (1900 LT) with a 5% depletion in electron content were found to attain an upward velocity of 200 m/sec at 1920 LT when the background electric field was 0.6 mV/m. Bubble altitude attained 447 km with an 88% depletion in electron content. In the absence of an ambient electric field, one hour was required for the vertical bubble velocity to reach 200 m/sec.

In associated research the ion densities of  $NO^+$ ,  $O_2^+$  and  $O^+$  were theoretically calculated by solving the coupled, time-dependent, non-linear ion continuity equations numerically and including the effects of production, loss and transport by diffusion and  $\bar{E} \times \bar{B}$  drift. Incorporation of a realistic vertical  $\bar{E} \times \bar{B}$  drift model which included a prereversal enhancement in upward drift, produced  $NO^+$ ,  $O_2^+$  and  $O^+$  density profiles which were found to be consistent with observations. The chemical reaction  $O_2^+ + N(^4S) \rightarrow NO^+ + O$  was found to act as a sink for  $O_2^+$  ions and source of  $NO^+$  as the F layer moved upward under the action of  $\bar{E} \times \bar{B}$  drift. Both the observations and calculations revealed that where  $NO^+$  was the dominant ion, the electron and ion densities were nearly constant in altitude, i.e. the plasma scale height became very large. The implications of this on the growth of large scale irregularities were presented in several publications.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Remote Lidar Measurement of Wind, Turbulence, and Convective Structure in the Planetary Boundary Layer
2. PRINCIPAL INVESTIGATOR: Dr. Edwin Eloranta  
Department of Meteorology  
University of Wisconsin  
Madison, WI 53706
3. INCLUSIVE DATES: 1 August 1980 - 30 September 1980
4. GRANT NUMBER: AFOSR-MIPR-80-00041 to U.S. Army Research Office
5. COSTS AND FY SOURCE: \$55,000, FY80
6. SENIOR RESEARCH PERSONNEL: Dr. J. Weinman
7. PUBLICATIONS:

"Lidar Measurements of Wind Velocity Profiles in the Boundary Layer," J. T. Sroga, E. W. Eloranta, and T. Barber, J. Appl. Meteor., 19, 598, (1980)

### 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This effort was designed to analyze lidar data obtained during a 1979 field project, test several planetary boundary layer (PBL) models against the reduced data sets, and refine the capabilities of observing winds by lidar. AFOSR support constituted the major portion of FY 80 funding initiating a three year project to be funded in succeeding years by ARO.

Lidar was used to measure wind and PBL depth for a 6-day period as part of the Central Illinois Rainfall Chemistry Experiment. The boundary layer depth measurements compare favorably with the depths observed in radiosonde temperature soundings. The model of Sroga was used to measure the speed, direction, and RMS variation of the wind. During the data analysis, an extension to this model was discovered which reduces the random errors in the measurement of the wind component along the lidar beam.

An extensive data set with over a thousand individual wind measurements was compiled from these lidar observations. During the daylight periods, lidar wind and depth measurements were normally made every 15 minutes. The lidar measurements of wind speed and direction are compared with radiosonde measurements and are found to be in close agreement.

This experiment included a period of 32 hours with nearly continuous lidar measurements. These observations show wind and PBL depth evolution over a complete diurnal cycle. The nocturnal portion of these measurements, when compared with kytoon measurements, show that a scanning lidar system can

measure nocturnal winds. The time-height cross sections of the nocturnal winds clearly show the transition from a daytime to a nighttime boundary layer.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Studies of the Morphology of the High Latitude Ionosphere
2. PRINCIPAL INVESTIGATOR: Dr. J. V. Evans  
Haystack Observatory  
Massachusetts Institute of Technology  
Westford, MA 01886
3. INCLUSIVE DATES: 1 October 1978 - 30 September 1980
4. CONTRACT NO: F19628-80-C-0002
5. COSTS AND FY SOURCE: \$53,431, FY79; \$71,274, FY80
6. SENIOR RESEARCH PERSONNEL:

R. H. Wand  
W. L. Oliver  
J. M. Holt

### 7. PUBLICATIONS:

"F-region Ion Temperature Enhancements Resulting from Joule Heating,"  
M. J. Baron and R. H. Wand, submitted to Geophys. Res. Letters.

### 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The aim of the project was to develop analysis techniques applicable to the incoherent-scatter radar data collected in a program of observations coordinated with flights of the AFGL Airborne Ionospheric Observatory (AIO) from Goose Bay, Labrador. The Air Force is interested in the propagation of HF radio waves over the pole for communications and surveillance purposes. The AIO flights provided data from various instruments (ionosonde, all-sky camera, all-sky imaging photometer, scanning photometer, spectrometer) that would contribute to the development of models of polar-cap electron density. The incoherent-scatter experiments consisted of repeated latitudinal scans (55 to 75 degrees magnetic latitude). These experiments measure the density, temperature, and motion of the electrons and ions, providing complementary wide-area coverage for the AIO measurements. The radar experiments were of a new format, and previously existing computer systems were not designed to analyze, display, or model these data effectively. The project sought funds to develop the necessary analysis software; to develop models of the electron density versus height, time, and latitude; and to study the physics of transport processes at high latitudes.

The initial results of this project mapped the electron-density spatial structure, including identification of the trough region of low electron density, and were received with enthusiasm by AFGL personnel. Data from magnetically quiet and disturbed days have been compared, and effects



during a solar eclipse have been observed. These results reveal a great deal of coupling between the ionosphere and magnetosphere at high latitudes. The competing effects of ionization by solar ultraviolet and particle precipitation, transport, and energy-dependent electron loss rates can only be resolved and understood from studies that provide the continuous time history of the large region in which these various processes are operating. Electric fields are seen to be very important in controlling high-latitude morphology. These fields, which are impressed upon the ionosphere from the earth's magnetosphere, give rise to horizontal transport of the F-region plasma at speeds up to 1 km/sec (2000 mph). In addition, by forcing the ions through the neutral air, they can increase the rate of ion-neutral chemical reactions and ionization loss. This effect appears to account for the deep troughs which have been observed, being formed in regions where the electric fields are particularly intense.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Shear Excitation of Atmospheric Gravity Waves

2. PRINCIPAL INVESTIGATOR: Dr. David C. Fritts  
Physical Dynamics, Inc.  
P.O. Box 3027  
Bellevue, WA 98009

3. INCLUSIVE DATES: 1 February 1981 - 31 January 1982

4. CONTRACT NUMBER: F49620-81-C-0009

5. COSTS AND FY SOURCE: \$39,818, FY81; \$19,910, FY82

6. PUBLICATIONS:

"A Mechanism of Gravity Wave Excitation Observable with Atmospheric Radars," D. C. Fritts, 20th AMS Conference on Radar Meteorology, 116 (1981).

"Shear Excitation of Atmospheric Gravity Waves," D. C. Fritts, J. Atmos. Sci., 39, 1936 (1982)

"The Transient Critical-Level Interaction in a Boussinesq Fluid," D. C. Fritts, J. Geophys. Res., 87, 7997 (1982).

"The Excitation of Atmospheric Gravity Waves by Unstable Shears," D. C. Fritts, Report PD-NW-82-260R, Physical Dynamics, Inc., Final Report, Contract F49620-81-C-0009 (1982)

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The principal objectives of this project were 1) a demonstration of the role of nonlinearity in the excitation of internal gravity waves through the interaction of rapidly growing Kelvin-Helmholtz (KH) instabilities and 2) an identification of the effects of the momentum redistribution resulting from unstable wave growth and decay. Both objectives were met through the application of a nonlinear numerical model to several idealized atmospheric shear profiles.

For profiles for which the KH mode exists, nonlinearity was found to permit the rapid excitation of a transient internal gravity wave of large amplitude via the interaction of two competing KH instabilities. The horizontal wavenumber and the frequency of the emerging wave were found to be determined by the difference of the horizontal wavenumbers and the frequencies of the two KH instabilities, similar to a resonant triad interaction. The vertical structure of other unstable modes of the system, but by the characteristics of the forcing KH instabilities themselves. Thus, whether or not the forced wave resembles an unstable mode for a particular shear profile depends only upon the similarity of the frequency and horizontal wavenumber of the forced wave and the unstable mode (if one exists).

Unstable modes that are propagating above and/or below an unstable shear differ from the KH mode (which is evanescent above and below) in several respects. Whereas the KH mode acts to stabilize an unstable shear by transporting mean momentum a short distance across the shear layer, propagating unstable modes may transport mean momentum to or through an unstable shear layer, resulting in an exchange of momentum between two remote levels of the atmosphere. In the case of unstable modes that are propagating only above or below a shear layer, mean momentum transported into the shear layer acts to stabilize the shear and cause the decay of the unstable mode. Unstable modes that are propagating above and below a source shear transport mean momentum into the shear layer until wave growth ceases. Thereafter, however, momentum is transported largely through the shear layer, permitting very gradual wave decay and causing potentially significant mean flow acceleration where the wave motion is dissipated. Possible results of this process include mean flow decelerations and jet and shear formation at other remote locations.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Global Atmospheric Waves; Mechanical Heating of the Lower Thermosphere
2. PRINCIPAL INVESTIGATOR: Dr. G. V. Groves  
Department of Physics and Astronomy  
University College London  
Gower Street  
London, WC1E 6BT, England
3. INCLUSIVE DATES: 1 January 1982 - 30 September 1982
4. GRANT NUMBER: AFOSR-82-0052
5. COSTS AND FY SOURCE: \$7,718 FY82
6. PUBLICATIONS:

"Hough Components of Water-Vapor Heating," G. V. Groves, J. Atmos. Terr. Phys., 44, 281 (1982).

"The Vertical Structure of Atmospheric Oscillations Formulated by Classical Tidal Theory," G. V. Groves, Planetary and Space Science, 30, 219 (1982).

"Hough Components of Ozone Heating," G. V. Groves, J. Atmos. Terr. Phys., 44, 111 (1982)

"Global Atmospheric Waves," G. V. Groves, Final Report, AFOSR Grant AFOSR-82-0052 (1982).

### 7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research effort was to account theoretically for the observed characteristics of atmospheric tides. The study of atmospheric tidal motions was considered relevant to the study of global atmospheric waves. Although comparisons between the available observations and calculation had revealed areas of general agreement, notable discrepancies were also found such as the findings that the amplitudes and phases of barometric oscillations were not well accounted for and that stratospheric tidal winds showed evidence of significant non-migrating and high-order modes for which adequate sources of generation were not identified. In this effort, tidal fields were evaluated using capabilities established only in the past few years.

Previously calculated height profiles of the (1,1,1) Hough components of heating due to water vapour and ozone absorption for mean January, April, July and October conditions were used to calculate by classical tidal theory the globally averaged flux of (1,1,1) energy propagating upwards at 80 km in a non-dissipating atmosphere. The results obtained reveal that

fluxes for January and July are lower than those for April and October, the relative decrease for January being about half that for July. The value for July is lower than for January on account of the greater Sun-Earth distance and January and July values are otherwise lower than those for April and October due to changes in the global distribution of water vapour in conjunction with the change of solar declination: the effect on the energy flux of changes in ozone heating between the respective dates was found to be relatively inconsequential.

Calculations carried out for two different sets of water vapour absorption coefficients revealed that the relative changes of flux for the four dates were insensitive to the particular absorption data adopted. On the other hand the values obtained for the undamped flux differed appreciably, being 1.34 and 2.68 mW/m<sup>2</sup> for the two sets of data. The extent to which these values were reduced by damping is uncertain, but previous calculations indicate a factor of four, in which case the present work yields a flux that is still well in excess of the energy requirement of 0.1 mW/m<sup>2</sup> estimated for maintaining a residual exospheric temperature of 500 K.

Compared with previous calculations, the yearly cycle defined by the January, April, July and October evaluations now shows a much closer similarity with that of the semi-annual variation of thermospheric air densities. The calculations in this study are however based on a number of simplifying assumptions, such as neglecting the background winds which might also contribute to the yearly cycle of the vertical energy flux. Further analysis is considered necessary before any definite conclusion might be reached on the physical origin of the semi-annual variation of thermospheric air densities.

Using similar techniques as for the (1,1,1) mode, energy flux propagating into the lower thermosphere in the (2,2,2) mode due to water vapour and ozone heating was estimated to have an equatorial value of close to 0.12 mW/m<sup>2</sup> with only a small annual variation. This value was noticeably smaller than the values of 0.3-0.4 mW/m<sup>2</sup> taken by Lindzen and Blake in their 1970 paper, the reduction arising mainly from the adoption of new ozone heating calculation.

By means of the one-dimensional heat conduction equation, Lindzen and Blake found that an upward tidal energy flux of 0.4 mW/m<sup>2</sup> would increase exospheric temperature by more than 200 K to about 1300 K for a noon EUV flux of 1.4 mW/m<sup>2</sup>. By a similar calculation, a tidal energy flux of 0.12 mW/m<sup>2</sup> with the same EUV flux is found to increase the exospheric temperature by 78 K. Such estimates apply to the equator and have neglected latitudinal heat conduction which would result in a much smaller global increase of exospheric temperature. If a tidal energy flux of 0.05 mW/m<sup>2</sup> is assumed as representative of the global mean energy flux, an exospheric temperature increase of 33 K is found. Although this is only an approximation, it indicates that the semidiurnal tide is a relatively minor source of thermospheric heating.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Analysis of NOAA Alaskan MST Radar System Data
2. PRINCIPAL INVESTIGATOR: Dr. Michael C. Kelley  
School of Electrical Engineering  
Cornell University  
Ithaca, NY 14853
3. INCLUSIVE DATES: 1 October 1979 - 30 September 1982
4. GRANT NUMBER: AFOSR-80-0020
5. COSTS AND FY SOURCE: \$51,000, FY80; \$59,447, FY81; \$61,854, FY82;
6. SENIOR RESEARCH PERSONNEL:

M. F. Larsen  
D. T. Farley

### 7. PUBLICATIONS:

"Turbulence Spectra in the Upper Troposphere and Lower Stratosphere at Periods Between 2 Hours and 40 Days," M. F. Larsen, M. C. Kelley, and K. S. Gage, J. Atmos. Sci., 39, 1035 (1982).

"VHF and UHF Doppler Radars as Tools for Synoptic Research," M. F. Larsen, and J. Rottger, Bull. Amer. Meteorol. Soc., 63, 996 (1982).

"Analysis of NOAA/Alaskan MST Radar Data," M. F. Larsen, M. C. Kelley, and D. T. Farley, Final Report, AFOSR Grant AFOSR-80-0020, Report No. AFOSR-TR-81-0859, (1981).

"Can a VHF Doppler Radar Provide Synoptic Wind Data?: A Comparison of 30 Days of Radar and Radiosonde Data," M. F. Larsen, Submitted to Mon. Wea. Rev., (1982).

### 8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research involved analysis of tropospheric and lower stratospheric wind data from the VHF Doppler radar located at Poker Flat, Alaska. Hourly averages of the winds for a 40 day period from the end of February to the beginning of April 1979 were used to investigate the turbulence spectra at periods from a few hours to a few days. We determined that a wavenumber power spectral slope of  $-5/3$  characterized the meteorological mesoscale. Earlier studies using other measurement techniques had pointed toward the same result, but the Poker Flat data set is by far the most complete so far available for such an investigation.

We also compared the radar winds averaged over various time intervals to the geostrophic wind calculated from a grid of geopotential height

values. The radiosonde pressure-surface height observations were subjected to the Cressman univariate objective analysis procedure to provide a grid of values suitable for estimating the synoptic scale geostrophic wind. Radar winds were also compared to the rawinsonde wind measurements from Fairbanks, 35 km southeast of the radar site. The goals of the research project were to provide independent estimates of the error of the rawinsonde wind measurements for synoptic applications, to determine the magnitude of the ageostrophic wind component, and to test a simple objective analysis method by comparing it to the estimate of the mean wind obtained by averaging the high time-resolution radar data. Cross-correlation coefficients between the wind and height fields were also calculated. The latter are of interest since they are used in a number of multivariate objective analysis schemes.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Investigation of Shear-Induced Turbulence by MST Radar

2. PRINCIPAL INVESTIGATORS: Dr. Gerald J. Romick  
Dr. Kolf Jayaweera  
Geophysical Institute  
University of Alaska  
Fairbanks, Alaska 99701

3. INCLUSIVE DATES: 1 October 1980 - 30 September 1982

4. GRANT NUMBER: AFOSR-80-0286

5. COSTS AND FY SOURCE: \$29,597, FY81; \$50,392, FY82

6. JUNIOR RESEARCH PERSONNEL: Steven A. Smith

7. PUBLICATIONS:

"Verification of WSFO Fairbanks Sigmets of Moderate or Greater Turbulence with Poker Flat MST Radar for the Period September 8, 1980 through March 31, 1981," S. A. Smith and R. R. Hoopes, Tech. Attachment, Borealis Briefs, Jan. 1982.

"Investigation of Clear Air Turbulence Using the Poker Flat MST Radar," S. A. Smith, M.S. Thesis, University of Alaska, May 1982.

"The Observation of Shear-Induced Turbulence by the Poker Flat MST Radar," S. A. Smith, G. J. Romick and K. Jayaweera, (Abstract) Transactions, AGU, 63, 338, (1982).

"MST Radar Observations of Shear Induced Turbulence," S. A. Smith, G. J. Romick, K. Jayaweera, and B. Balsley, submitted to J. Geophys. Res., October 1982.

"Investigation of Shear-Induced Turbulence by MST Radar," G. J. Romick, K. Jayaweera, and S. A. Smith, Geophysical Institute, University of Alaska, Final Report, Grant AFOSR-80-0286 (1982).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The aim of this project was to utilize data from the Poker Flat MST radar for the study of the development and evolution of clear air turbulence (CAT). The study had a twofold purpose: to understand the basic relationship between wind velocity, shear and the development of turbulence and to determine the capability of the MST in the detection and forecast of episodes of clear air turbulence. Both of these areas have been studied and significant information obtained even though the delayed



completion of the Poker Flat MST Radar in the fall of 1982 restricted the spatial resolution, initially expected to be 300 meters, to only 2.2 km during most of the grant period. Thus, basic information close to the scale size of the turbulent layer was unavailable during the whole grant period. Nevertheless, the information obtained from the coarser resolution operation has been extremely interesting. The data used in this study were obtained over the period from September 1980 through March 1981 when the radar was operating with one quarter of the final system and over a 13-hour period at 750 meter resolution with three quarters of the final system in operation in February 1982.

The measured Doppler shift, due to the projection of the motion of the refractive irregularities in the direction of the radar beam, was converted to horizontal wind speed by assuming zero vertical motion. This zero vertical wind assumption becomes more valid as the averaging time increases and is less valid in the high resolution data set. However, in consideration of the small value for the vertical component the measured radial speed is mainly due to horizontal motion of the atmosphere.

The measured signal strengths were converted to estimates of  $C_n^2$  the radio refractivity turbulence structure constant. The resultant estimates of  $C_n^2$  were used to infer turbulence intensity at scale sizes corresponding to half the radar wavelength which is 3 m for the Poker Flat radar. The signal strengths were obtained from the Doppler power spectra. The relevant quantity used in the  $C_n^2$  calculation was the signal-to-noise ratio (S/N) from each height in each beam. The actual power returned to the radar was obtained by scaling the S/N to the estimated cosmic noise power that was received by the radar.

The method used to examine the relationship between shears and turbulence has been to compute time-lagged cross-correlation coefficients using various length time series of wind speed, wind shear, and  $C_n^2$  measurements. The results indicate that there exists a good correlation between  $C_n^2$  and wind speed over long periods of time but that the correlation between  $C_n^2$  and wind shear is strongest only for hour-long periods and 750 m spatial resolution. No correlation was found for constant altitude intervals, only with those at fixed height increments above the level of maximum wind. With reference to sample volumes at the level of maximum wind and 2.2 km above, there was little or no correlation of the wind shear between these levels with the average  $C_n^2$  of the two levels. There is a significant correlation of about 0.4 near zero lag for the correlation of the wind shear between the volumes 2.2 and 4.4 km above the maximum wind level and the average value of  $C_n^2$  over those two volumes.

The implication of the correlations of these different time series is that the wind shears that lead directly to turbulence can be resolved only with short time and small spatial sampling intervals. The observed correlations between shears are strongest at lags of about 10 to 30 minutes only over short time periods (order of an hour) and the shears are probably averaged out over longer periods of many hours or days.

The Fairbanks office of the National Weather Service (NWS) forecasts clear air turbulence to be in the region between the tropopause and the level of maximum wind when that level is below the tropopause and the Richardson number is about 1. The Poker Flat data examined to date has supported the forecasts. A  $C_n^2$  magnitude of  $1 \times 10^{-17} \text{ m}^{-2/3}$  over a 2.2 km layer has been associated with moderate CAT on the basis of six-pilot reports of CAT in the vicinity of Poker Flat. Over the six months study period, 18 CAT episodes were forecast by the NWS and all were identified or closely associated with the appearance of turbulence exceeding the threshold value of  $C_n^2$  on the MST radar. Through the analysis it was found that approximately 0.03 of the 2.2 km high radar sample volume was turbulent. This agrees well with the 0.01 to 0.1 factor previously found by others..

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

## COMPLETED PROJECT SUMMARY

1. TITLE: Project Definition Study for National STORM Program
2. PRINCIPAL INVESTIGATOR: Dr. Stanley Ruttenberg  
Office of Scientific Program Development  
University Corporation for Atmospheric  
Research  
Boulder, CO 80307
3. INCLUSIVE DATES: 6 July 1981 - 31 January 1982
4. GRANT NUMBER: AFOSR-ISSA-81-00040 (to NOAA)
5. COSTS AND FY SOURCE: \$10,000, FY81
6. PUBLICATIONS:  
  
"The National STORM Program - Framework for a Plan," University Corporation for Atmospheric Research Report to National Oceanic and Atmospheric Administration, (Vol 1) Contract NA81RAC00123 (1982).  
  
"The National STORM Program - Scientific Bases and Major Objectives," University Corporation for Atmospheric Research Report to National Oceanic and Atmospheric Administration, (Vol 2), Contract NA81RAC00123 (1982).

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The overall objective of the study was to identify particular deficiencies in understanding of meteorological phenomena, with primary emphasis on the mesoscale, and to develop plans for alleviating those deficiencies through coordinated research projects. A related objective was the development of plans for optimum utilization of high-technology remote and in situ sensing devices and for the training of operational weather personnel in the use of this equipment. The two-volume report addresses the scientific and organizational aspects of a major series of coordinated field programs. These review the state of knowledge of mesoscale weather systems in different regions of the United States and the status of theoretical studies and numerical models of these systems, and discuss current capability and needs in observations, short-range forecasting, and education. Finally, recommendations are set forth for field programs in the central, eastern, and western United States in the 1980's and early 1990's.

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